# Supporting Information

## Palladium-catalyzed cascade cyclization of allylamine-tethered alkylidenecyclopropanes: facile access to iodine/difluoromethylene- and perfluoroalkyl-containing benzazepine scaffolds

Liu-Zhu Yu,[a] Zi-Zhong Zhu,[a] Xu-Bo Hu,[a] Xiang-Ying Tang[b] and Min Shi*[a,b]

[a]*Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Mei Long Road, Shanghai 200237 China.*

[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032 China.*

*Mshi@mail.sioc.ac.cn. Fax: 86-21-64166128*

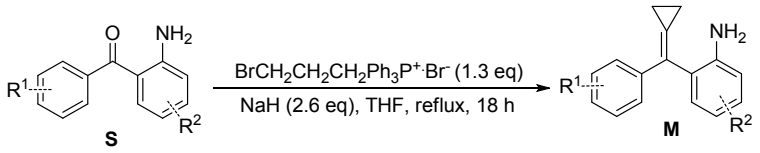
### Contents

**General remarks**

Unless otherwise indicated, all glassware was oven dried by a heat gun before use and all reactions were performed under an atmosphere of argon. THF was distilled from sodium (Na) under argon (Ar) atmosphere. 1,4-dioxane was super-dry purchased from Aldrich. All other solvents were purchased from Adamas and used as received. Isatoic anhydride and other materials obtained from commercial suppliers were used without further purification. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. All NMR spectra were recorded on an AM-300 or AM-400 spectrophotometers in $CDCl_3$, NMR chemical shifts are reported in ppm referenced to the solvent peaks of $CDCl_3$ (7.26 ppm for $^1H$ and 77.0 ppm for $^{13}C$, respectively). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in $cm^{-1}$. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Mass spectra were recorded by ESI, and HRMS were measured on a HP-5989 instrument.

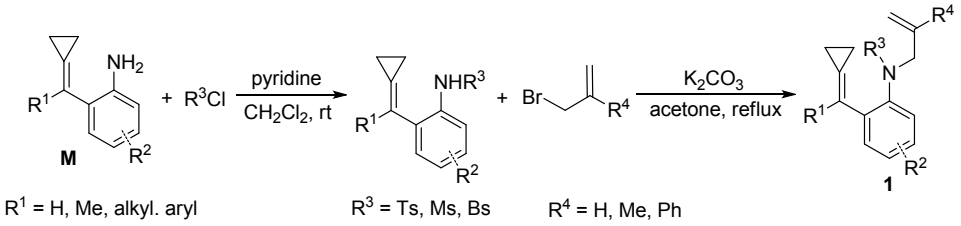
**General procedure for the synthesis of ACPs**

**Compounds M** were prepared according to previously reported work[1] and the corresponding spectroscopic data are consistent with those in reported literature. 2-aminobenzophenones **S** were prepared from isatoic anhydride according to the related literature.[2]



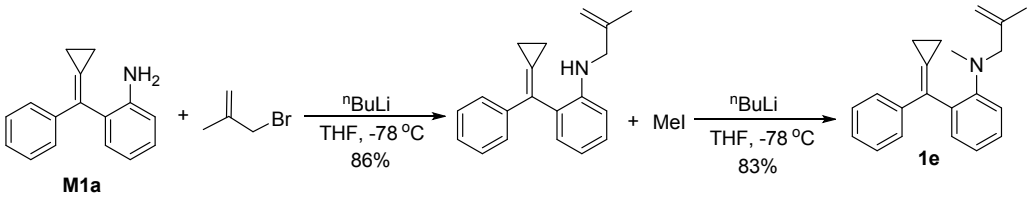

A solution of 3-bromopropyltriphenylphosphonium bromide (5.96 g, 13 mmol) and NaH (624 mg, 26 mmol) in THF (15 mL) was stirred at 70 $^{o}$C under $N_2$ for 12 h. Afterwards compound **S** (10 mmol) in THF (10 mL) was added and the reaction solution was stirred at 70 $^{o}$C for another 12 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 60 / 1 to 40 / 1) to afford the products **M** in moderate yields.

**General procedure for the synthesis of substrates 1**




**M** (2.0 mmol, 1.0 equiv) was dissolved in dry $CH_2Cl_2$ (4.0 mL), then pyridine (2.4 mmol, 1.5 equiv) and sulfonyl chloride $R^3Cl$ (3.0 mmol, 1.2 equiv) were added respectively and the resulting reaction mixture was stirred at room temperature for 12 h. The reaction mixture was quenched by $CuSO_4$ solution and extracted with $CH_2Cl_2$ for 3 times. The combined organic layer was washed with brine and dried over anhydrous $Na_2SO_4$. After filtration, the filtrate was concentrated under reduced pressure and the residue was not purified for the next step directly. The crude product was dissolved in acetone (4.0 mL), then $K_2CO_3$ (4.0 mmol, 2.0 equiv) and 2-methylallylbromide (2.4 mmol, 1.2 equiv) were added respectively and the resulting reaction mixture was stirred under reflux overnight. Upon completion, the reaction mixture was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **1** in good yields.

The synthesis of substrate **1e**:

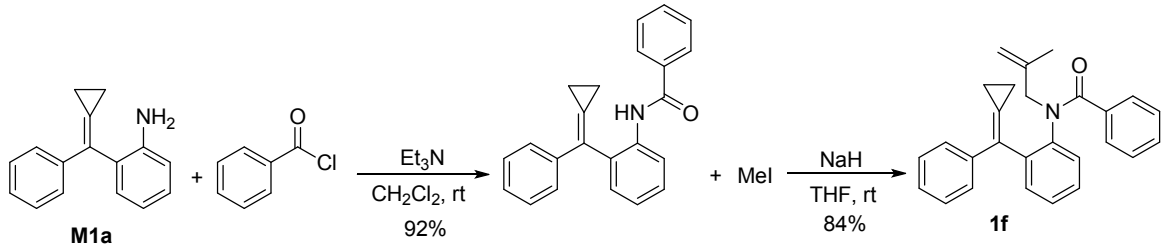



To a 150 mL flask charged with **M1a** (2.0 mmol, 1.0 equiv) and THF (20 mL) was added $^n$BuLi (2.5 M in hexanes, 2.0 mmol, 1.0 equiv) dropwise at -78 °C under Ar atmosphere. The resulting solution was allowed to stir at the same temperature for 30 min. The 2-methylallylbromide (2.4 mmol, 1.2 equiv) was introduced in one portion at -78 °C and the reaction mixture was allowed to stir for 16 h at room temperature. Upon completion, water was added to the solution to quench the reaction. After remove the most of THF solvent under reduced pressure, the mixture was extracted with EtOAc (3 x 10 mL). The combined organic layer was dried over $Na_2SO_4$ and concentrated.

The residue was purified by silica gel flash chromatography (eluent: petroleum ether) to afford *ortho*-allylaminoaryl ACP in 86% yield.

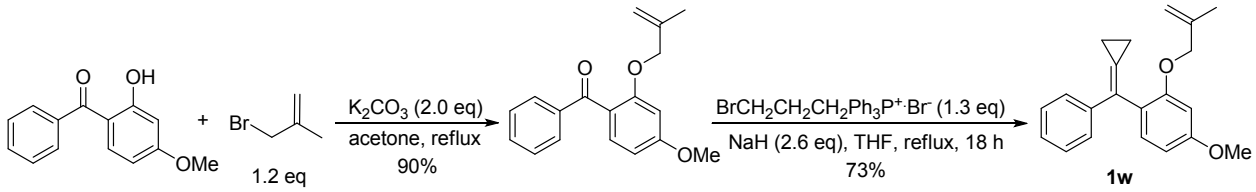
The obtained *ortho*-allylaminoaryl alkylidenecyclopropane (1.0 mmol, 1.0 equiv) was dissolved in THF (5.0 mL) at -78 °C under Ar atmosphere and $^{n}$BuLi (2.5 M in hexanes, 1.0 mmol, 1.0 equiv) was added dropwise. The solution was allowed to stir at the same temperature for 30 min. Iodomethane (1.2 mmol, 1.2 equiv) was introduced in one portion at -78 °C and the reaction mixture was allowed to stir for 16 h at room temperature. Upon completion, water was added to the solution to quench the reaction. After remove the most of THF solvent under reduced pressure, the mixture was extracted with EtOAc (3 x 10 mL). The combined organic layer was dried over $Na_2SO_4$ and concentrated. The residue was purified by silica gel flash chromatography (eluent: petroleum ether) to afford **1e** in 83% yield.

The synthesis of substrate **1f**:



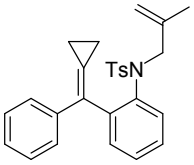

A solution of compound **M1a** (2.0 mmol, 1.0 equiv) in $CH_2Cl_2$ (5.0 mL) was stirred at 0 °C under $N_2$. Then $Et_3N$ (3.0 mmol, 1.5 equiv) and benzoyl chloride (2.4 mmol, 1.2 equiv) were added dropwise respectively and the resulting mixture was warmed to room temperature and stirred overnight. Upon completion, the mixture was evaporated to remove the solvent. The residue dissolved in THF (4.0 mL) was added to NaH (3.0 mmol, 1.5 equiv) in THF (5.0 mL) at 0 °C dropwise and the reaction mixture was stirred for 30 min. Afterwards 2-methylallylbromide (3.0 mmol, 1.5 equiv) was added in one portion and the reaction mixture was stirred overnight at room temperature. The reaction was quenched by water and extracted with DCM for 3 times. The combined organic layer was washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10/1) to afford the product **1f**.

The synthesis of substrate **1z**:

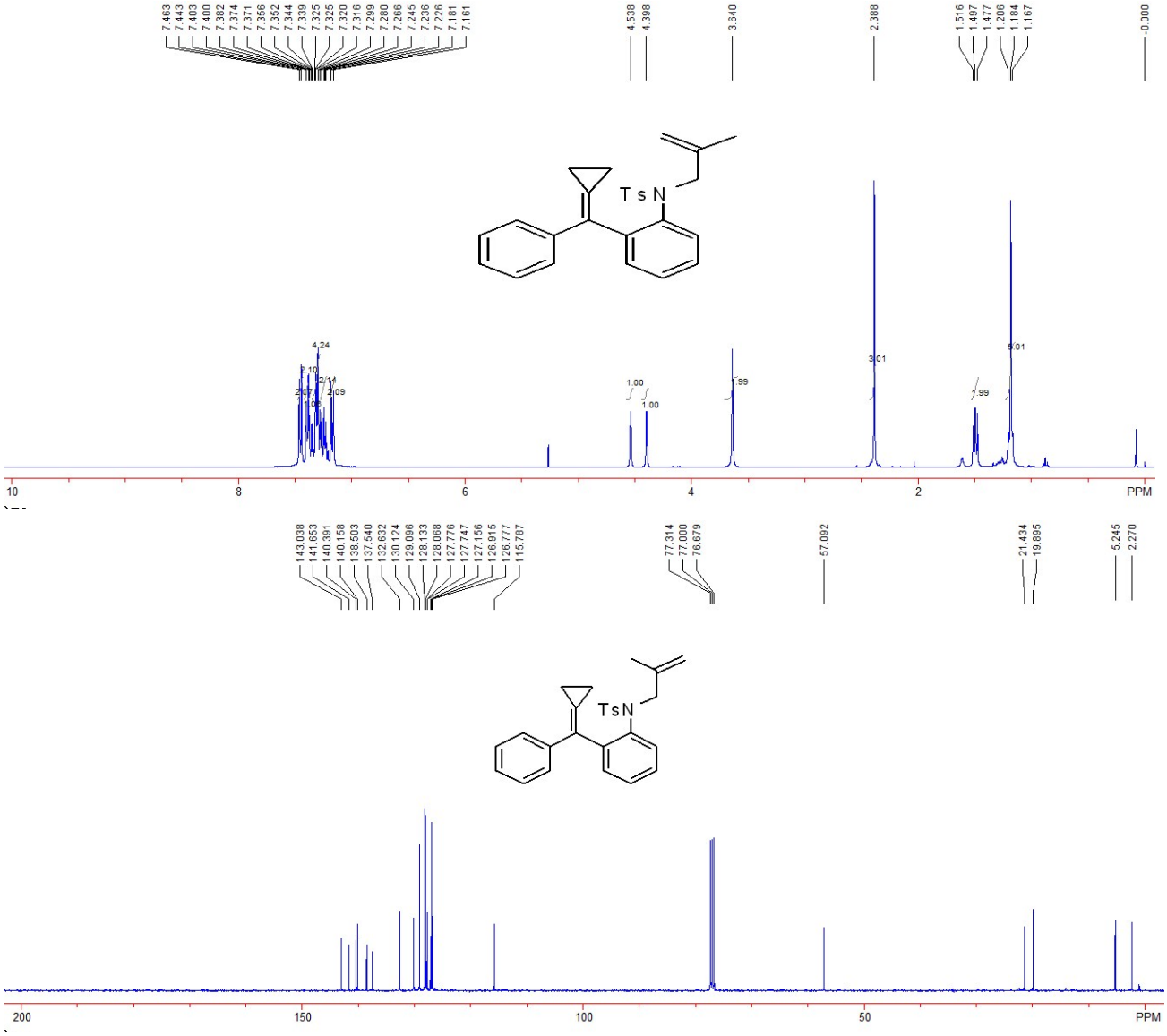


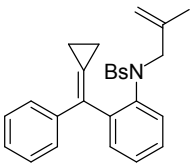

To a solution of oxybenzone (2.0 mmol, 1.0 equiv) in acetone (5.0 mL) was added $K_2CO_3$ (4.0 mmol, 2.0 equiv) and allyl bromide (2.4 mmol, 1.2 equiv), the resulting mixture was stirred under reflux for 2 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the allylic oxybenzone in 90% yield. A solution of obtained allylic oxybenzone, 3-bromopropyltriphenylphosphonium bromide (2.6 mmol, 1.3 equiv) and NaH (5.2 mmol, 2.6 equiv) in THF (15 mL) was stirred at 70 $^oC$ under $N_2$ for 12 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 40 / 1) to afford **1z** in 73% yield.

**Spectroscopic data for substrates 1**

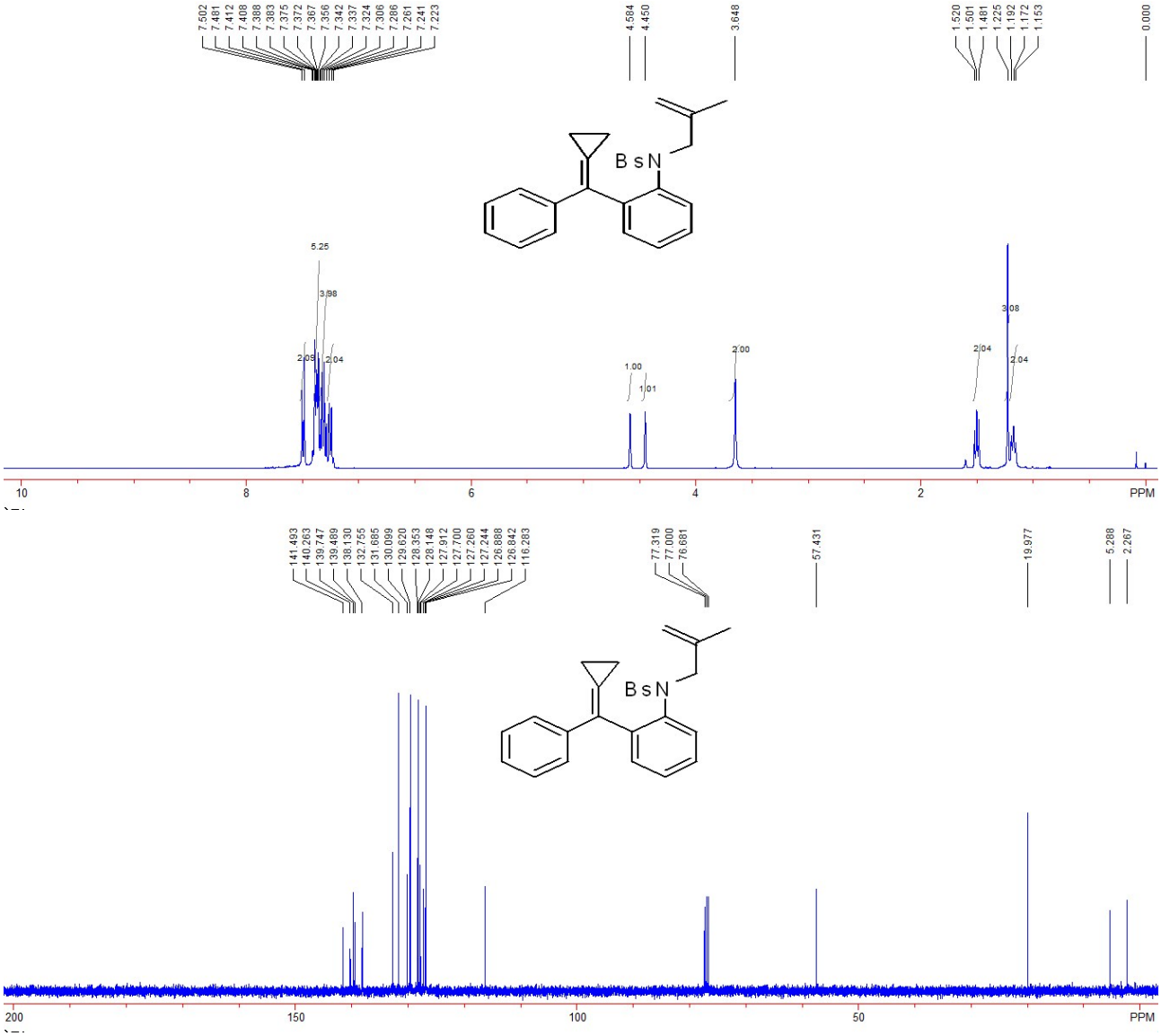


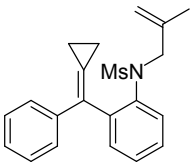

**Compound 1a**: 755 mg, 88%, A white solid, m.p. 125-127 $^{o}$C; IR ($CH_2Cl_2$): ν 3055, 2974, 2920, 1597, 1494, 1445, 1341, 1159, 1092, 906, 859, 816, 767, 695 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17-1.21 (m, 5H), 1.50 (t, 2H, *J* = 7.6 Hz), 2.39 (s, 3H), 3.64 (s, 2H), 4.40 (s, 1H), 4.54 (s, 1H), 7.17 (d, 2H, *J* = 8.0 Hz), 7.21-7.32 (m, 6H), 7.34-7.40 (m, 3H), 7.45 (d, 2H, *J* = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.2, 19.9, 21.4, 57.1, 115.8, 126.8, 126.9, 127.2, 127.7, 127.8, 128.07, 128.13, 129.1, 130.1, 132.6, 137.5, 138.5, 140.2, 140.4, 141.7, 143.0; MS (ESI) *m/z*: 447.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{31}N_2O_2S^+$ requires: 447.2101, Found: 447.2103.



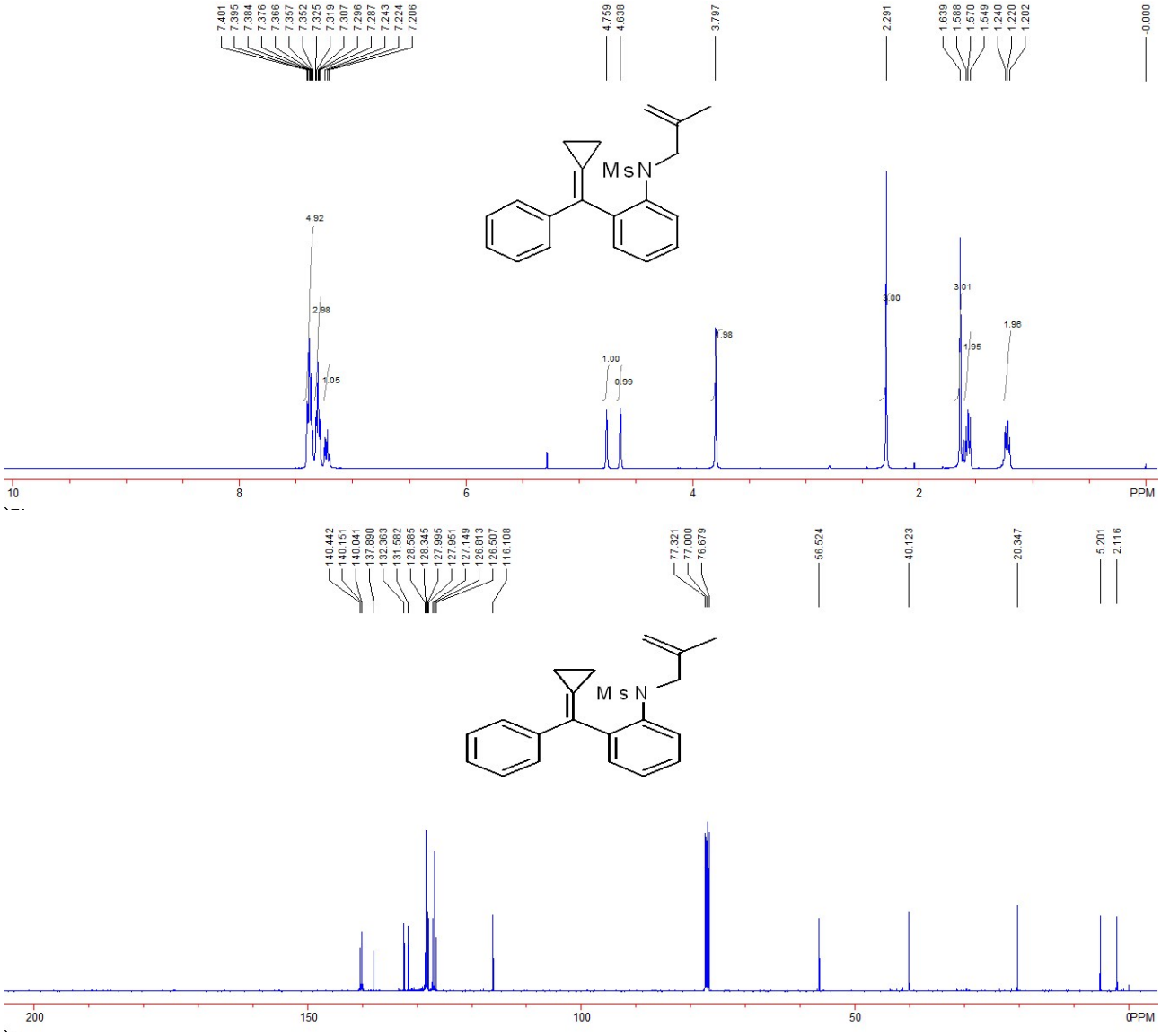


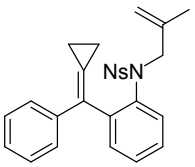

**Compound 1b**: 838 mg, 85%, A white solid, m.p. 128-130 °C; IR ($CH_2Cl_2$): ν 3059, 3029, 2973, 1574, 1472, 1448, 1389, 1355, 1162, 1089, 1069, 1009, 822, 746, 695 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (t, 2H, $J$ = 7.6 Hz), 1.23 (s, 3H), 1.50 (t, 2H, $J$ = 7.6 Hz), 3.65 (s, 2H), 4.45 (s, 1H), 4.58 (s, 1H), 7.22-7.26 (m, 2H), 7.29-7.34 (m, 4H), 7.36-7.41 (m, 5H), 7.49 (d, 2H, $J$ = 8.4 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.3, 20.0, 57.4, 116.3, 126.8, 126.9, 127.2, 127.3, 127.7, 127.9, 128.1, 128.4, 129.6, 130.1, 131.7, 132.8, 138.1, 139.5, 139.7, 140.3, 141.5; MS (ESI) *m/z*: 511.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{28}BrN_2O_2S^+$ requires: 511.1049, Found: 511.1048.



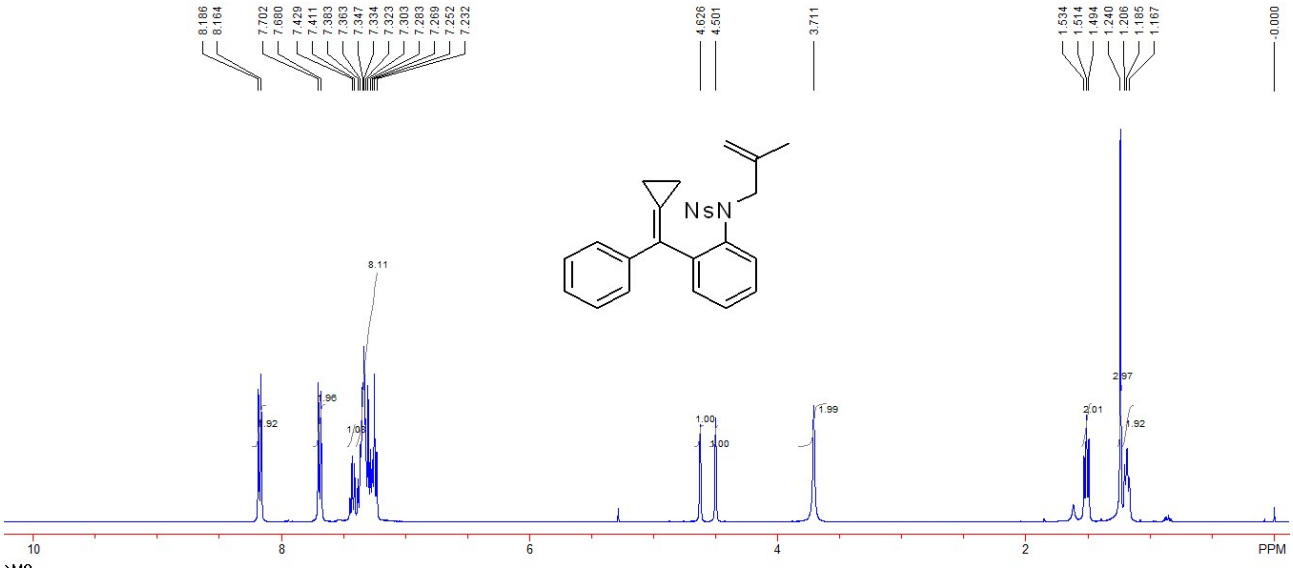


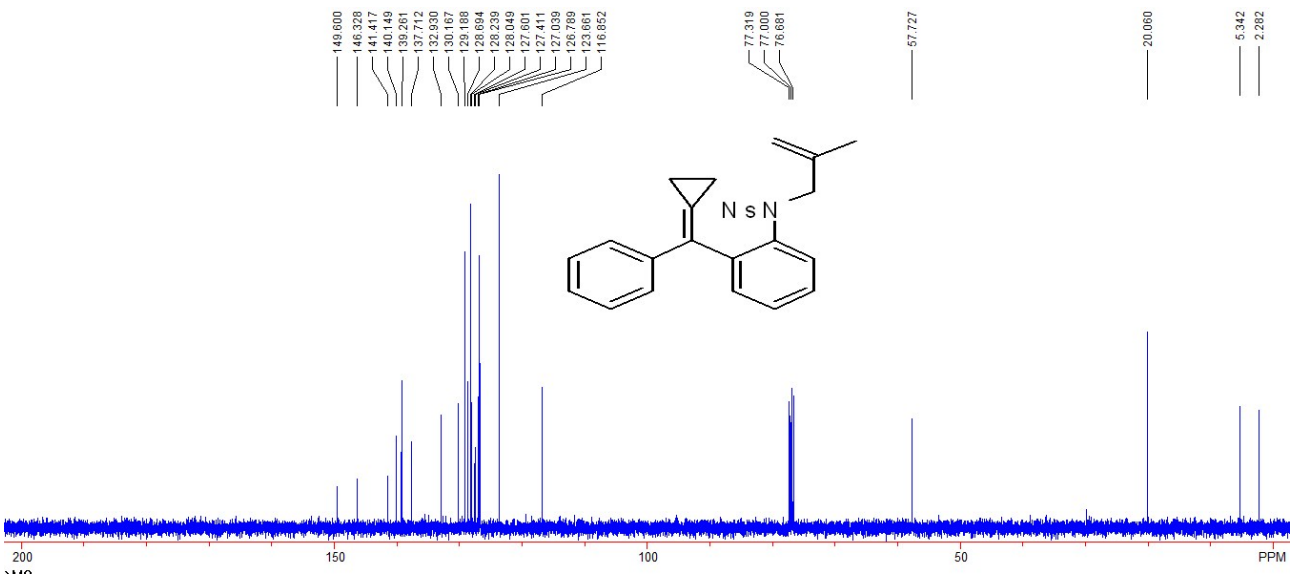

**Compound 1c**: 558 mg, 79%, A white solid, m.p. 89-91 $^{o}$C; IR ($CH_2Cl_2$): ν 3029, 2974, 2929, 1714, 1598, 1486, 1446, 1331, 1148, 1079, 961, 906, 865, 766, 753, 697 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.22 (t, 2H, *J* = 7.6 Hz), 1.57 (t, 2H, *J* = 7.6 Hz), 1.64 (s, 3H), 2.29 (s, 3H), 3.80 (s, 2H), 4.64 (s, 1H), 4.76 (s, 1H), 7.20-7.24 (m, 1H), 7.29-7.32 (m, 3H), 7.35-7.40 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.1, 5.2, 20.3, 40.1, 56.5, 116.1, 126.5, 126.8, 127.1, 127.95, 128.00, 128.3, 128.6, 131.6, 132.4, 137.9, 140.0, 140.2, 140.4; MS (ESI) *m/z*: 371.2 (M+$NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{27}N_2O_2S^+$ requires: 371.1788, Found: 371.1788.

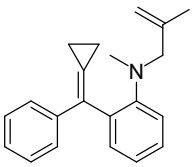




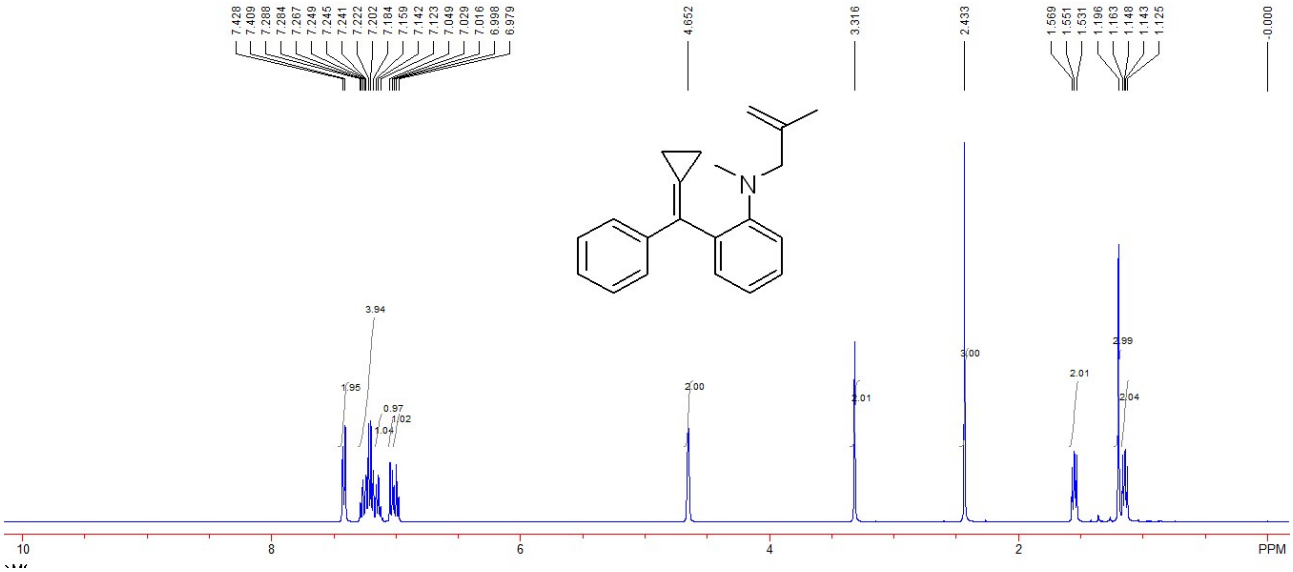

**Compound 1d**: 764 mg, 83%, A white solid, m.p. 117-119 °C; IR ($CH_2Cl_2$): ν 3045, 2981, 2915, 1530, 1444, 1349, 1307, 1164, 1091, 853, 750, 743, 697 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.19 (t, 2H, *J* = 8.0 Hz), 1.24 (s, 3H), 1.51 (t, 2H, *J* = 8.0 Hz), 3.71 (s, 2H), 4.50 (s, 1H), 4.63 (s, 1H), 7.23-7.28 (m, 8H), 7.43 (t, 1H, *J* = 7.6 Hz), 7.69 (d, 2H, *J* = 8.8 Hz), 8.18 (d, 2H, *J* = 8.8 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.3, 20.1, 57.7, 116.9, 123.7, 126.8, 127.0, 127.4, 127.6, 128.0, 128.2, 128.7, 129.2, 130.2, 132.9, 137.7, 139.3, 140.1, 141.4, 146.3, 149.6; MS (ESI) *m/z*: 478.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{28}N_3O_4S^+$ requires: 478.1796, Found: 478.1795.

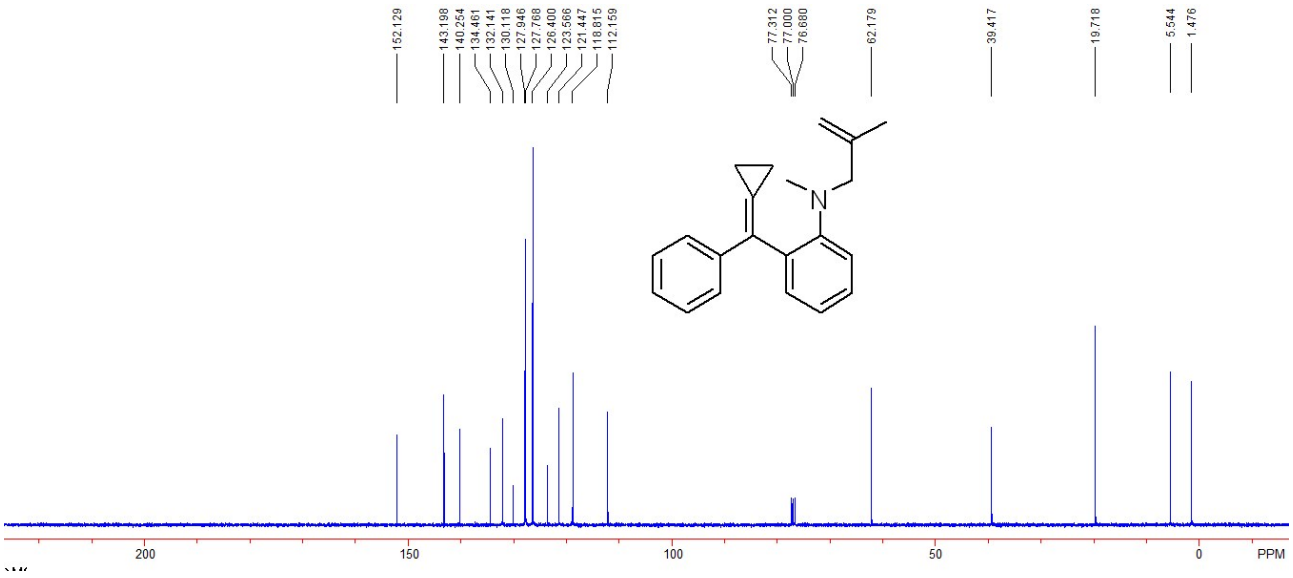


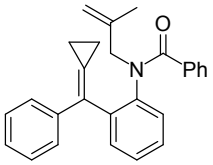





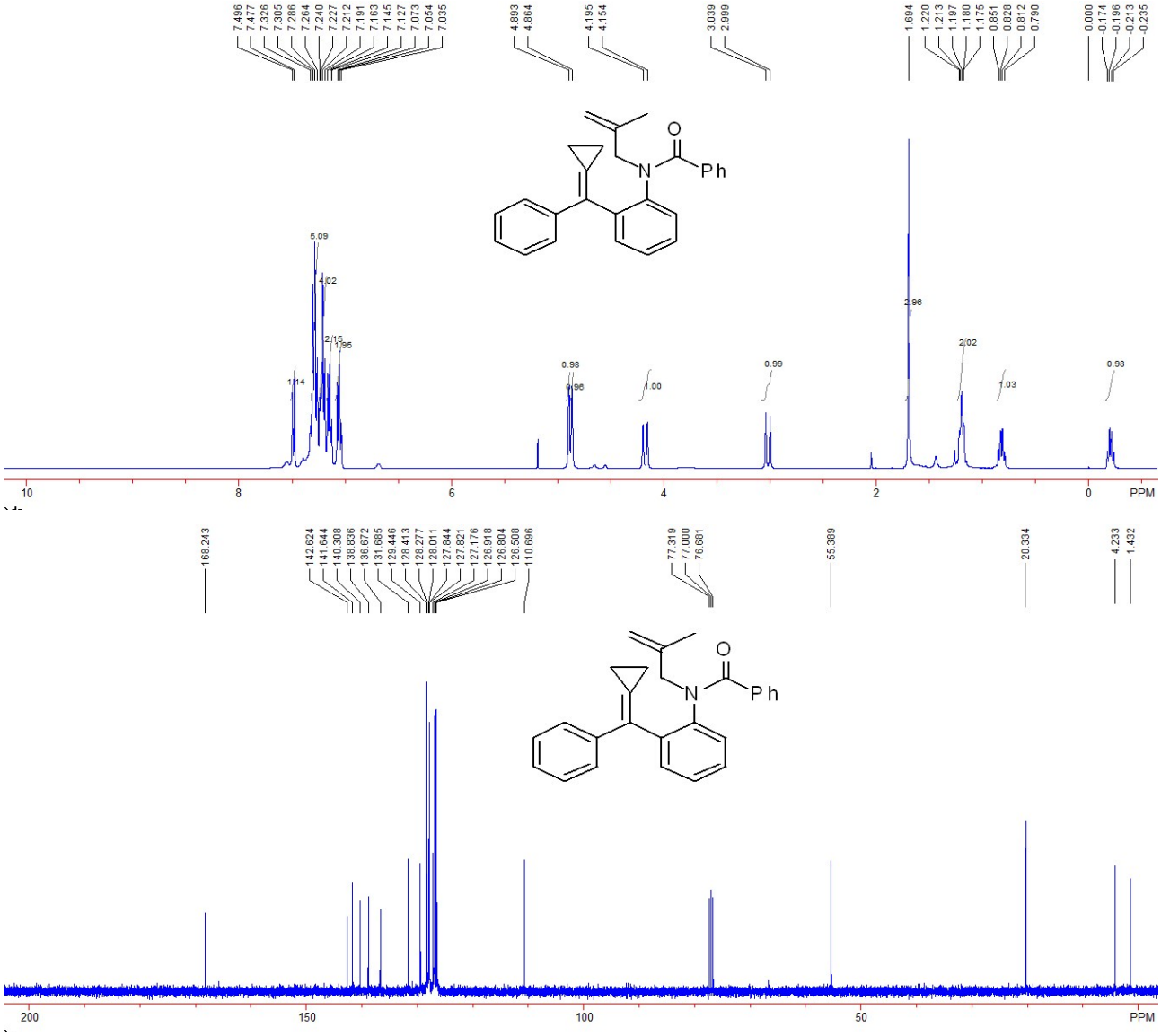
**Compound 1e**: 410 mg, 71%, A colorless oil; IR ($CH_2Cl_2$): ν 3054, 2970, 2791, 1593, 1488, 1445, 1353, 1227, 1177, 1105, 1046, 932, 898, 747, 763, 693 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.13-1.16 (m, 2H), 1.20 (s, 3H), 1.53-1.57 (m, 2H), 2.43 (s, 3H), 3.32 (s, 2H), 4.65 (brs, 2H), 7.00 (t, 1H, $J$ = 7.6 Hz), 7.04 (d, 1H, $J$ = 8.0 Hz), 7.14 (d, 1H, $J$ = 7.6 Hz), 7.18-7.29 (m, 4H), 7.42 (d, 2H, $J$ = 7.6 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 1.5, 5.5, 19.7, 39.4, 62.2, 112.2, 118.8, 121.4, 123.6, 126.4, 127.8, 127.9, 130.1, 132.1, 134.5, 140.3, 143.2, 152.1; MS (ESI) *m/z*: 290.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{24}N^+$ requires: 290.1905, Found: 290.1903.

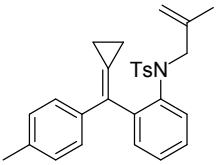


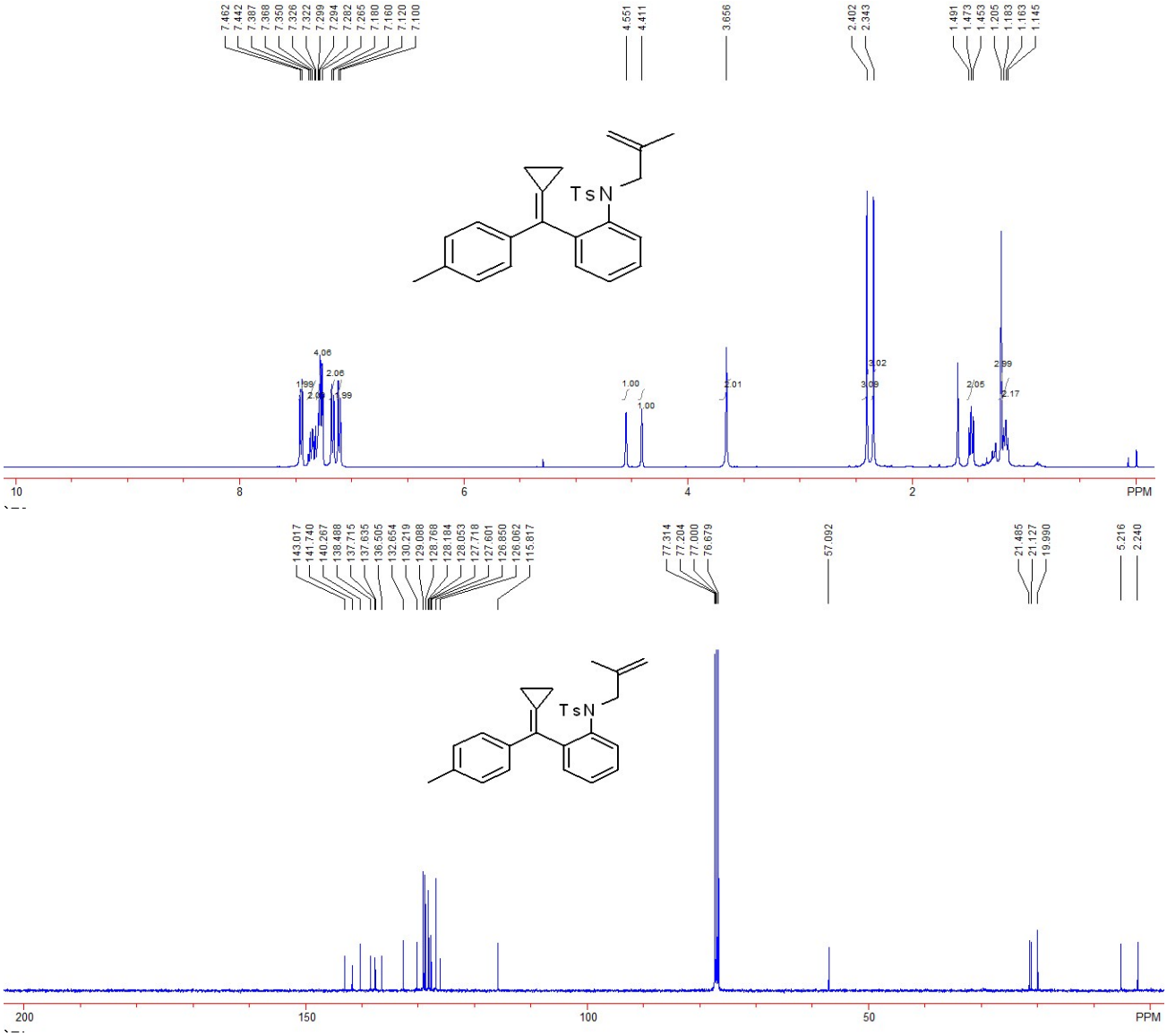


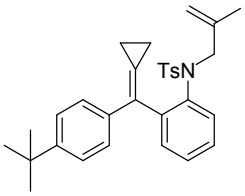

**Compound 1f**: 584 mg, 77%, A white solid, m.p. 168-170 $^{o}$C; IR ($CH_2Cl_2$): ν 3056, 3023, 2973, 1647, 1597, 1486, 1447, 1376, 1313, 1297, 1179, 902, 766, 752, 734, 696 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ -0.24--0.17 (m, 1H), 0.79-0.85 (m, 1H), 1.18-1.22 (m, 2H), 1.69 (s, 3H), 3.02 (d, 1H, *J* = 16 Hz), 4.17 (d, 1H, *J* = 16 Hz), 4.86 (s, 1H), 4.89 (s, 1H), 7.05 (t, 2H, *J* = 7.6 Hz), 7.15 (t, 2H, *J* = 7.6 Hz), 7.19-7.24 (m, 4H), 7.26-7.33 (m, 5H), 7.49 (d, 1H, *J* = 7.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 1.4, 4.2, 20.3, 55.4, 110.7, 126.5, 126.8, 126.9, 127.2, 127.82, 127.84, 128.0, 128.3, 128.4, 129.4, 131.7, 136.7, 138.8, 140.3, 141.6, 142.6, 168.2; MS (ESI) *m/z*: 380.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{26}NO^+$ requires: 380.2009, Found: 380.2010.



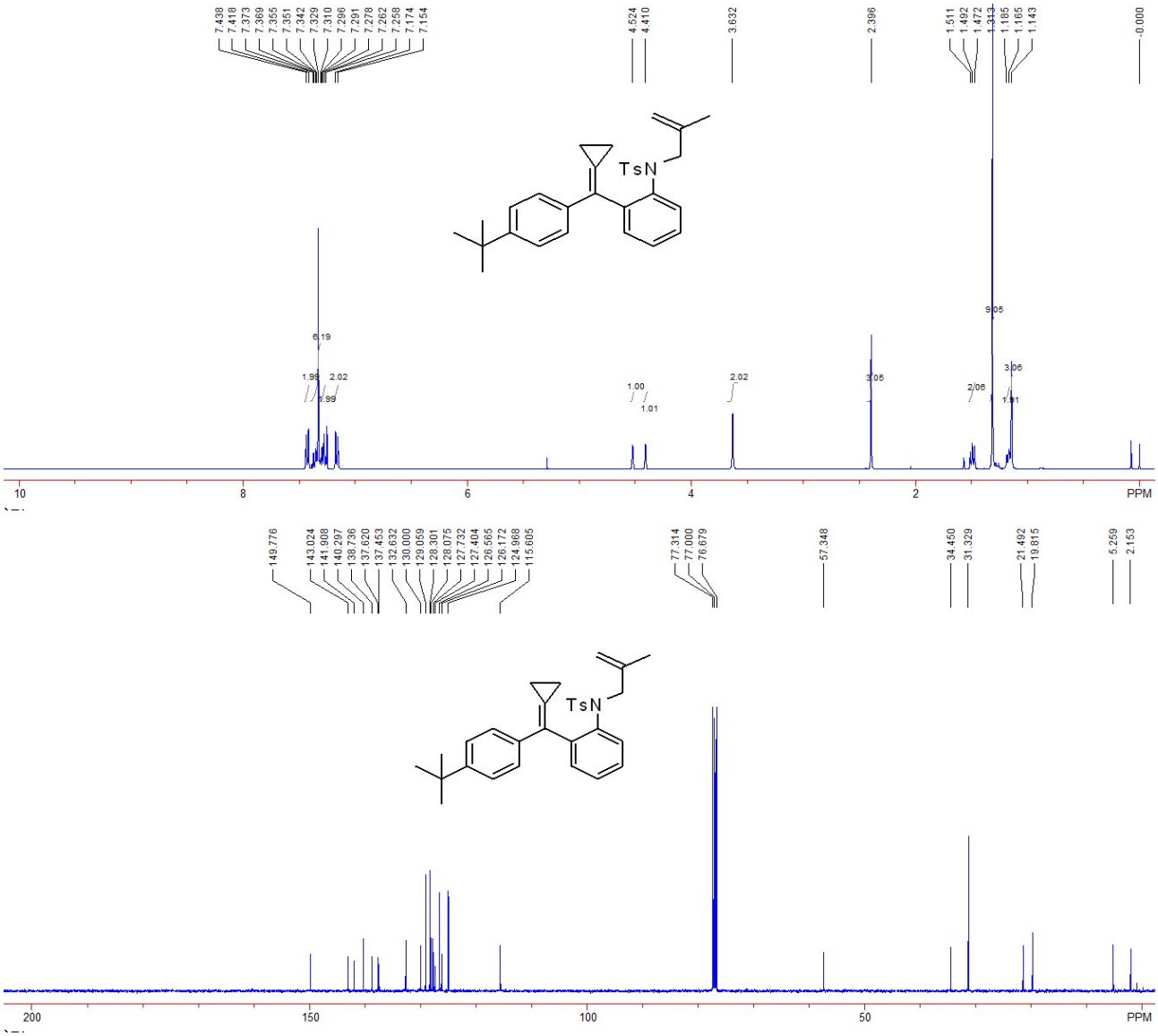


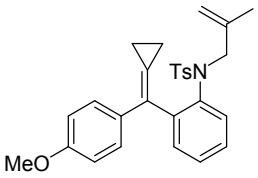

**Compound 1g**: 745 mg, 84%, A white solid, m.p. 130-132 $^{o}$C; IR ($CH_2Cl_2$): ν 2972, 2922, 2862, 1597, 1510, 1485, 1443, 1340, 1157, 1092, 907, 859, 815, 737, 698 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.16 (t, 2H, *J* = 7.6 Hz), 1.21 (s, 3H), 1.47 (t, 2H, *J* = 7.6 Hz), 2.34 (s, 3H), 2.40 (s, 3H), 3.66 (s, 2H), 4.41 (s, 1H), 4.55 (s, 1H), 7.11 (d, 2H, *J* = 8.0 Hz), 7.17 (d, 2H, *J* = 8.0 Hz), 7.26-7.31 (m, 4H), 7.32-7.39 (m, 2H), 7.45 (d, 2H, *J* = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.2, 20.0, 21.1, 21.5, 57.1, 115.8, 126.1, 126.9, 127.2, 127.7, 128.1, 128.2, 128.8, 129.1, 130.2, 132.7, 136.5, 137.6, 137.7, 138.5, 140.3, 141.7, 143.0; MS (ESI) *m/z*: 444.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{30}NO_2S^+$ requires: 444.1992, Found: 444.1992.



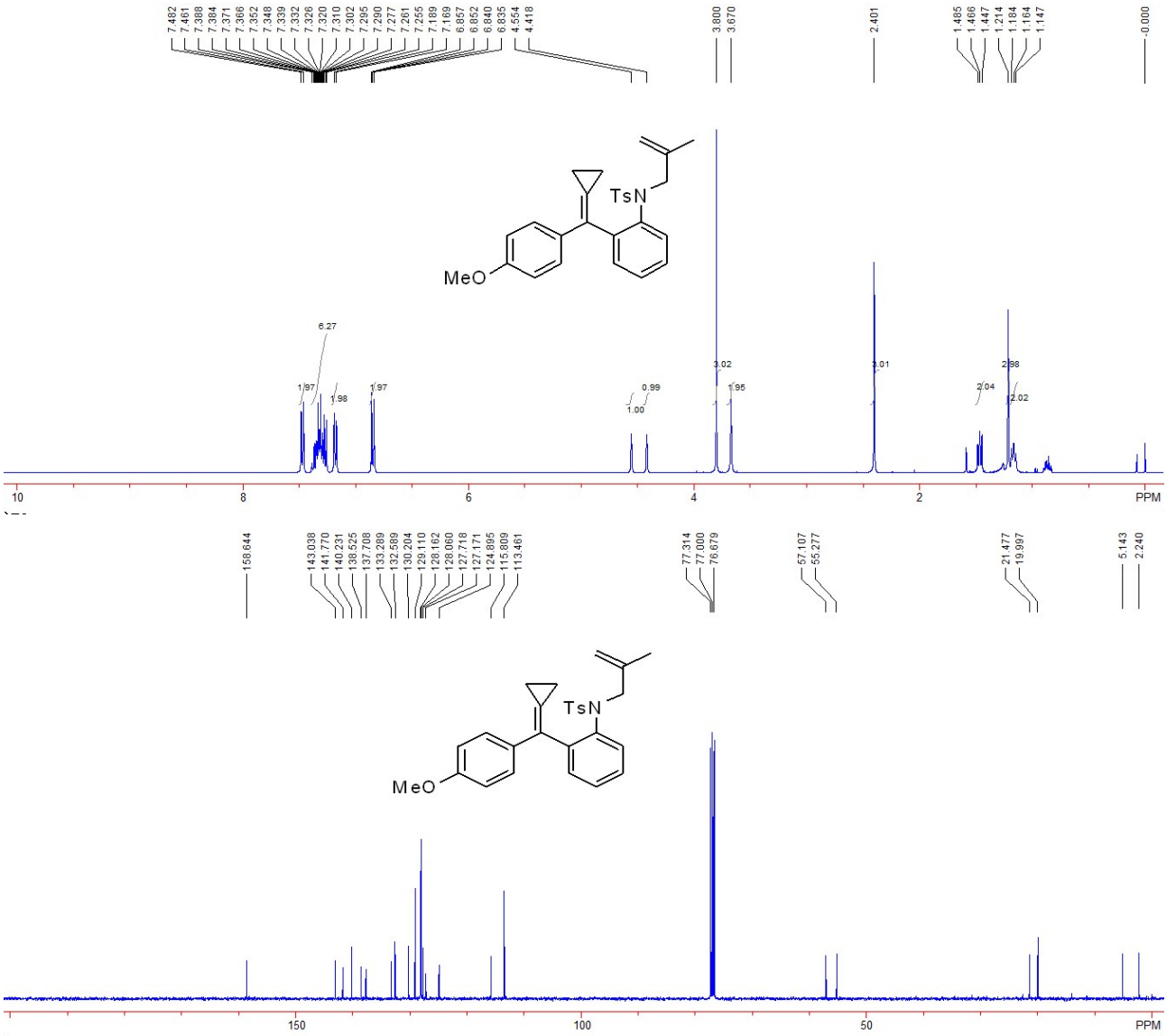


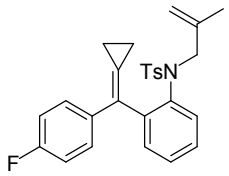

**Compound 1h**: 728 mg, 75%, A white solid, m.p. 140-142 °C; IR ($CH_2Cl_2$): ν 2966, 2898, 2862, 1442, 1354, 1166, 1093, 1046, 1021, 885, 821, 767, 721, 685 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.14 (s, 3H), 1.17 (t, 2H, *J* = 7.6 Hz), 1.31 (s, 9H), 1.49 (t, 2H, *J* = 7.6 Hz), 2.40 (s, 3H), 3.63 (s, 2H), 4.41 (s, 1H), 4.52 (s, 1H), 7.16 (d, 2H, *J* = 8.0 Hz), 7.26-7.30 (m, 2H), 7.31-7.37 (m, 6H), 7.43 (d, 2H, *J* = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.3, 19.8, 21.5, 31.3, 34.5, 57.3, 115.6, 125.0, 126.2, 126.6, 127.4, 127.7, 128.1, 128.3, 129.1, 130.0, 132.6, 137.5, 137.6, 138.7, 140.3, 141.9, 143.0, 149.8; MS (ESI) *m/z*: 503.3 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{39}N_2O_2S^+$ requires: 503.2727, Found: 503.2728.



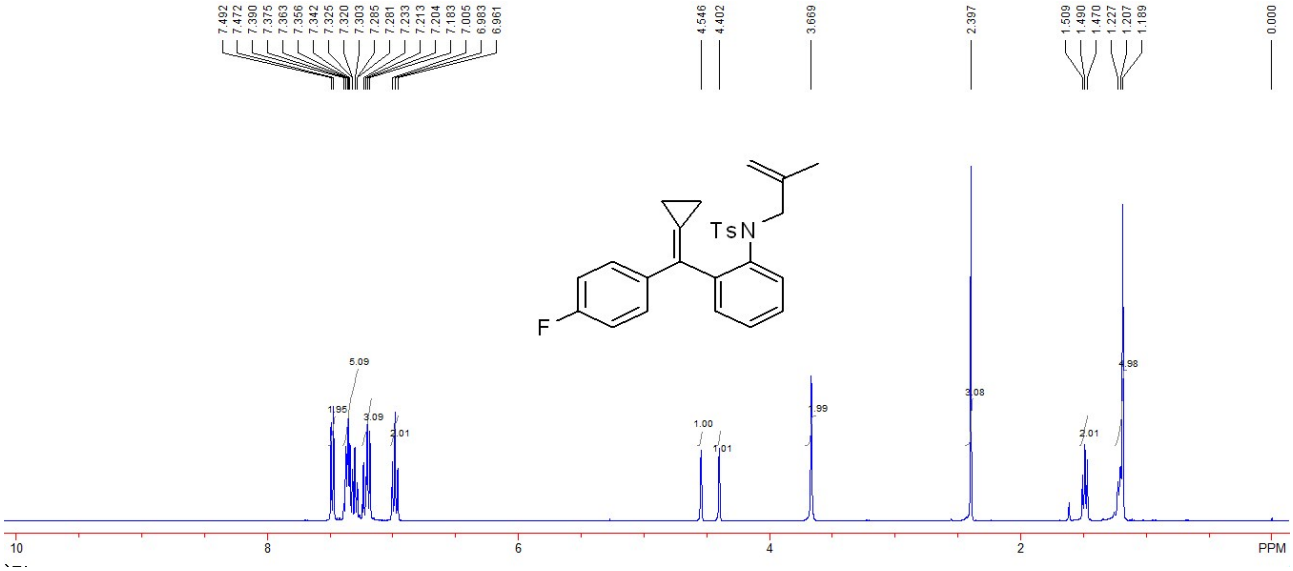


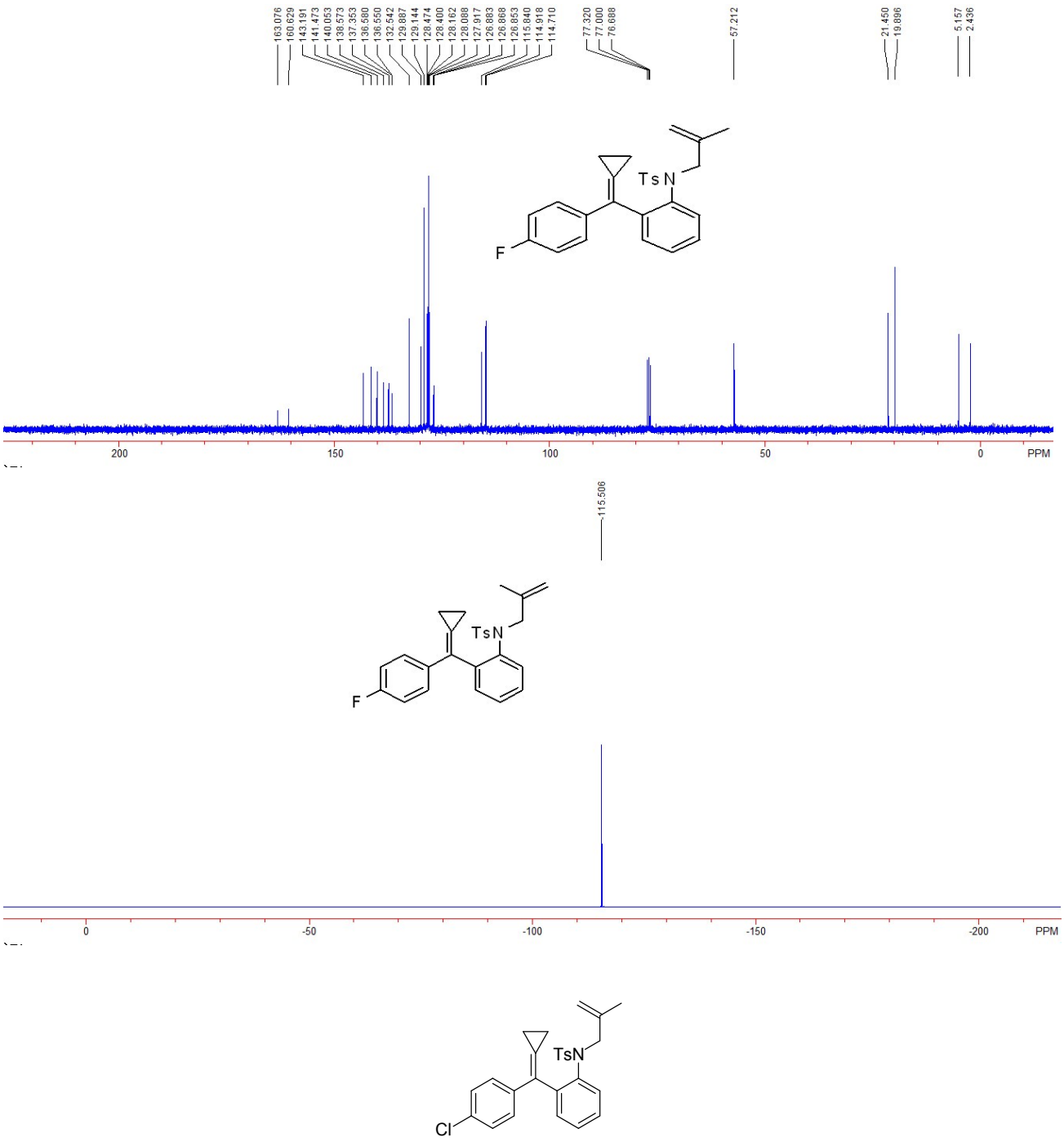

**Compound 1i**: 808 mg, 88%, A white solid, m.p. 120-122 $^{o}$C; IR ($CH_2Cl_2$): ν 2972, 2829, 2837, 1606, 1509, 1485, 1443, 1342, 1302, 1249, 1176, 1159, 1093, 1032, 908, 830, 790, 658 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.16 (t, 2H, $J$ = 7.6 Hz), 1.21 (s, 3H), 1.47 (t, 2H, $J$ = 7.6 Hz), 2.40 (s, 3H), 3.67 (s, 2H), 3.80 (s, 3H), 4.42 (s, 1H), 4.55 (s, 1H), 6.85 (dd, 2H, $J_1$ = 6.8 Hz, $J_2$ = 2.0 Hz), 7.18 (d, 2H, $J$ = 8.0 Hz), 7.26-7.39 (m, 6H), 7.47 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.1, 20.0, 21.5, 55.3, 57.1, 113.5, 115.8, 124.9, 127.2, 127.7, 128.1, 128.2, 129.1, 130.2, 132.6, 133.3, 137.7, 138.5, 140.2, 141.8, 143.0, 158.6; MS (ESI) *m/z*: 460.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{30}NO_3S^+$ requires: 460.1941, Found: 460.1932.



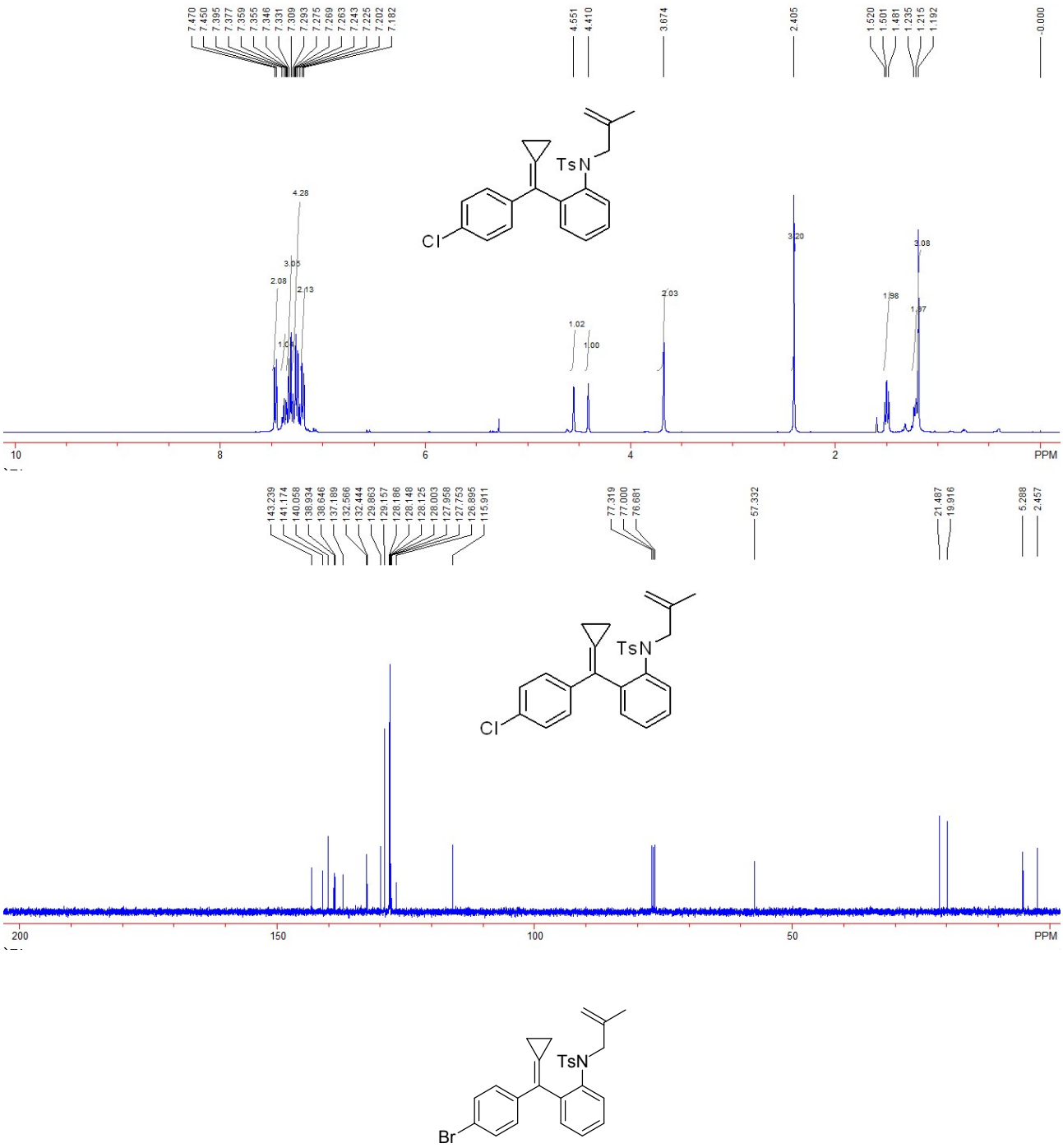



**Compound 1j**: 608 mg, 68%, A white solid, m.p. 115-117 $^{o}$C; IR ($CH_2Cl_2$): ν 3067, 2974, 2920, 1597, 1506, 1443, 1342, 1222, 1157, 1092, 1019, 833, 815, 657 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.19 (s, 3H), 1.21 (t, 2H, $J$ = 7.6 Hz), 1.49 (t, 2H, $J$ = 7.6 Hz), 2.40 (s, 3H), 3.67 (s, 2H), 4.40 (s, 1H), 4.55 (s, 1H), 6.98 (t, 2H, $J$ = 8.8 Hz), 7.18-7.23 (m, 3H), 7.28-7.39 (m, 5H), 7.48 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.4, 5.2, 19.9, 21.5, 57.2, 114.8 (d, $J_{C-F}$ = 20.8 Hz), 115.8, 126.86 (d, $J_{C-F}$ = 1.5 Hz), 126.88, 127.9, 128.1, 128.2, 128.4 (d, $J_{C-F}$ = 8.1 Hz), 129.1, 129.9, 132.5, 136.6 (d, $J_{C-F}$ = 3.0 Hz), 137.4, 138.6, 140.1, 141.5, 143.2, 161.9 (d, $J_{C-F}$ = 244.7 Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -115.5 (s); MS (ESI) *m/z*: 448.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{27}FNO_2S^+$ requires: 448.1741, Found: 448.1742.

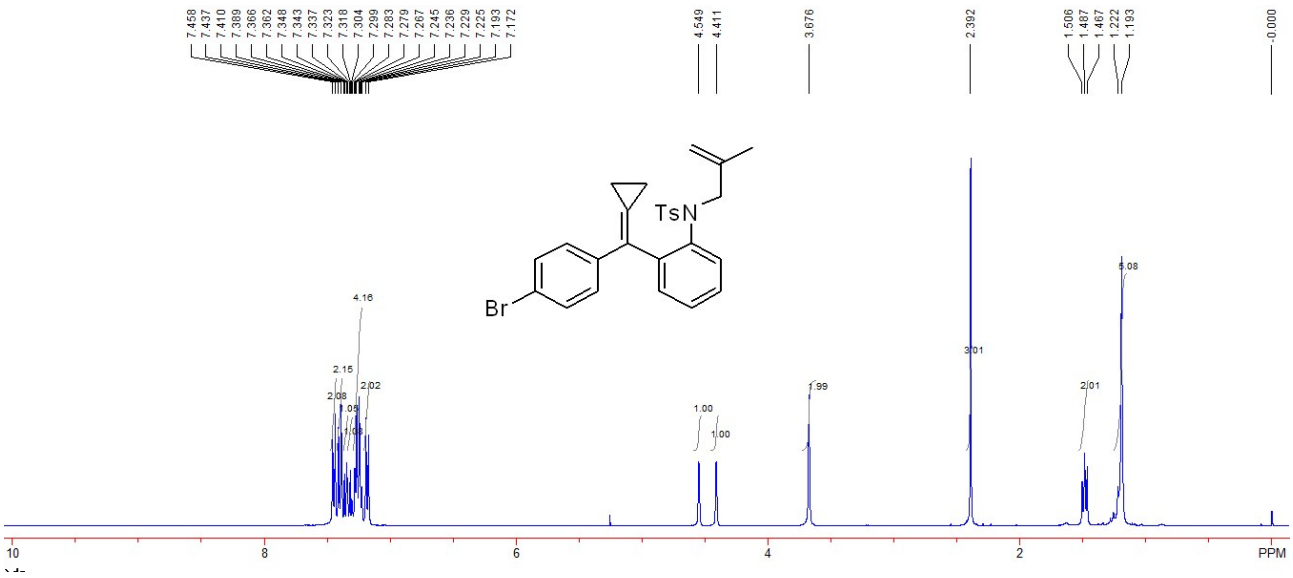


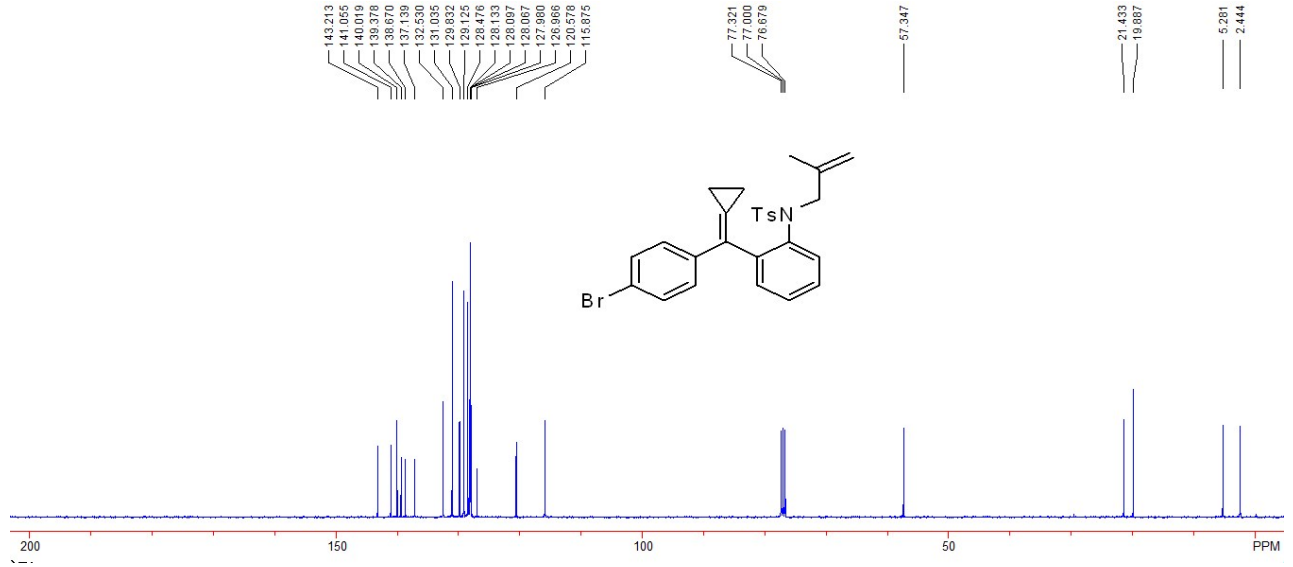


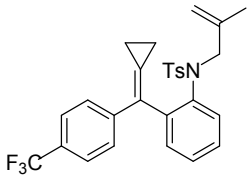

**Compound 1k**: 629 mg, 68%, A white solid, m.p. 128-130 $^{o}$C; IR ($CH_2Cl_2$): ν 3067, 2973, 2924, 2854, 1597, 1490, 1444, 1344, 1159, 1091, 1012, 907, 816, 756, 655 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.19 (s, 3H), 1.22 (t, 2H, $J$ = 7.6 Hz), 1.50 (t, 2H, $J$ = 7.6 Hz), 2.41 (s, 3H), 3.67 (s, 2H), 4.41 (s, 1H), 4.55 (s, 1H), 7.19 (d, 2H, $J$ = 8.0 Hz), 7.23-7.29 (m, 4H), 7.31-7.36 (m, 3H), 7.37-7.40 (m, 1H), 7.46 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.5, 5.3, 19.9, 21.5, 57.3, 115.9, 126.9, 127.8, 127.96, 128.00, 128.13, 128.15, 128.2, 129.2, 129.9, 132.4, 132.6, 137.2, 138.6, 138.9, 140.1, 141.2, 143.2; MS (ESI) *m/z*: 481.2 (M+$NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{30}ClN_2O_2S^+$ requires: 481.1711, Found: 481.1711.




**Compound 1l**: 791 mg, 78%, A white solid, m.p. 131-133 $^{o}$C; IR ($CH_2Cl_2$): ν 2972, 2924, 2879, 1486, 1449, 1346, 1159, 1090, 1046, 880, 815, 654 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.19-1.22 (m, 5H), 1.49 (t, 2H, *J* = 7.6 Hz), 2.39 (s, 3H), 3.68 (s, 2H), 4.41 (s, 1H), 4.55 (s, 1H), 7.18 (d, 2H, *J* = 8.4 Hz), 7.23-7.30 (m, 4H), 7.32-7.37 (m, 2H), 7.40 (d, 2H, *J* = 8.4 Hz), 7.45 (d, 2H, *J* = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.4, 5.3, 19.9, 21.4, 57.3, 115.9, 120.6, 127.0, 128.0, 128.07, 128.10, 128.13, 128.5, 129.1, 129.8, 131.0, 132.5, 137.1, 138.7, 139.4, 140.0, 141.2, 143.2; MS (ESI) *m/z*: 525.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{30}BrN_2O_2S^+$ requires: 525.1206, Found: 525.1205.

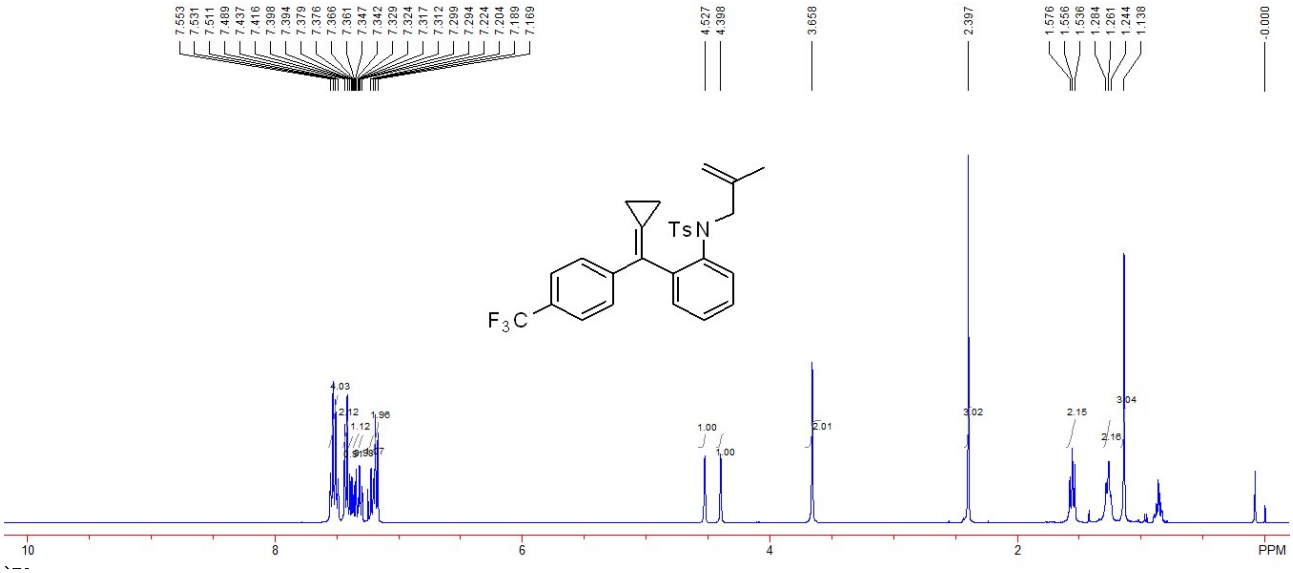


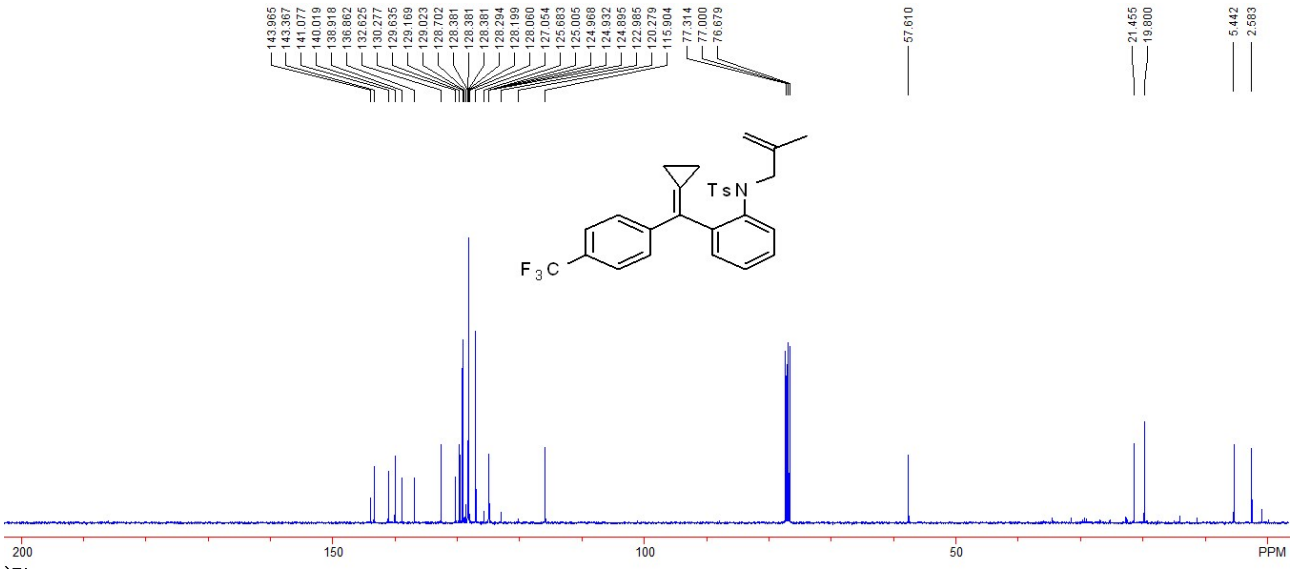



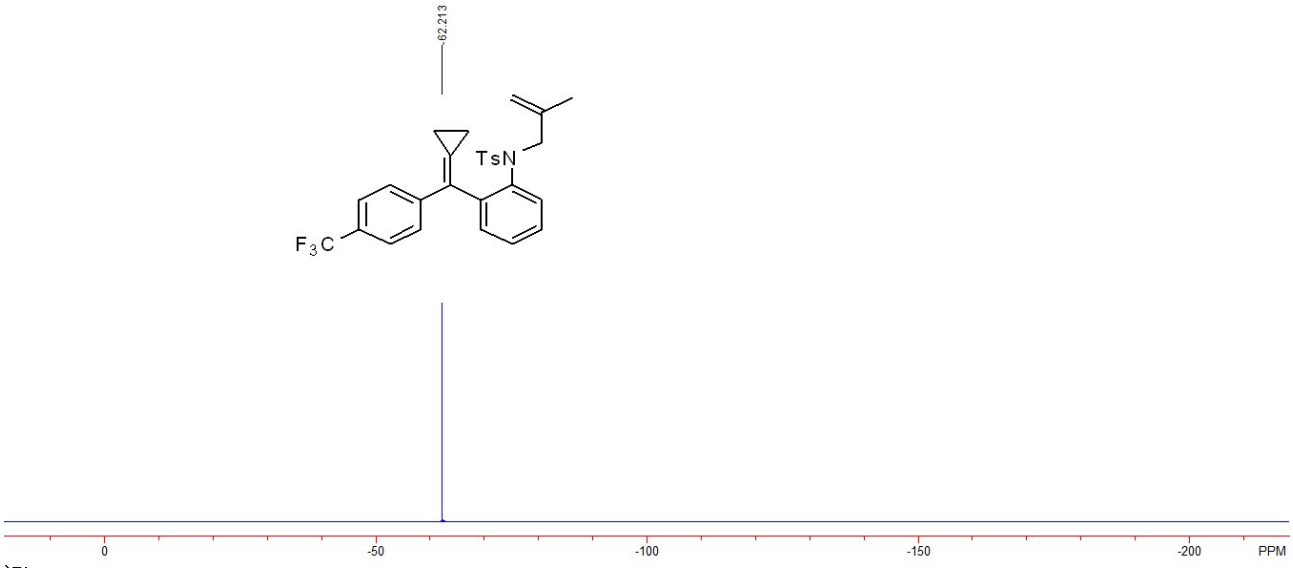



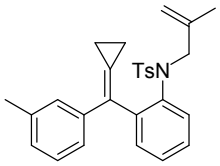

**Compound 1m**: 666 mg, 67%, A white solid, m.p. 105-107 $^{o}$C; IR ($CH_2Cl_2$): ν 3065, 2975, 2920, 1615, 1486, 1444, 1324, 1161, 1119, 1071, 1017, 909, 832, 816, 737, 655 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.14 (s, 3H), 1.26 (t, 2H, $J$ = 8.0 Hz), 1.56 (t, 2H, $J$ = 8.0 Hz), 2.40 (s, 3H), 3.66 (s, 2H), 4.40 (s, 1H), 4.53 (s, 1H), 7.18 (d, 2H, $J$ = 8.0 Hz), 7.21 (d, 1H, $J$ = 8.0 Hz), 7.31 (td, 1H, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz), 7.35 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz), 7.39 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz), 7.43 (d, 2H, $J$ = 8.4 Hz), 7.49-7.55 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.6, 5.4, 19.8, 21.5, 57.6, 115.9, 124.3 (q, $J_{C\text{-}F}$ = 269.8 Hz), 125.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 127.1, 128.2, 128.3, 128.5 (q, $J_{C\text{-}F}$ = 32.1 Hz), 129.2, 129.6, 130.3, 132.6, 136.9, 138.9, 140.0, 141.1, 143.4, 144.0; $^{19}$F NMR (376

MHz, $CDCl_3$, $CFCl_3$): δ -62.2 (s); MS (ESI) *m/z*: 515.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{30}F_3N_2O_2S^+$ requires: 515.1975, Found: 515.1977.

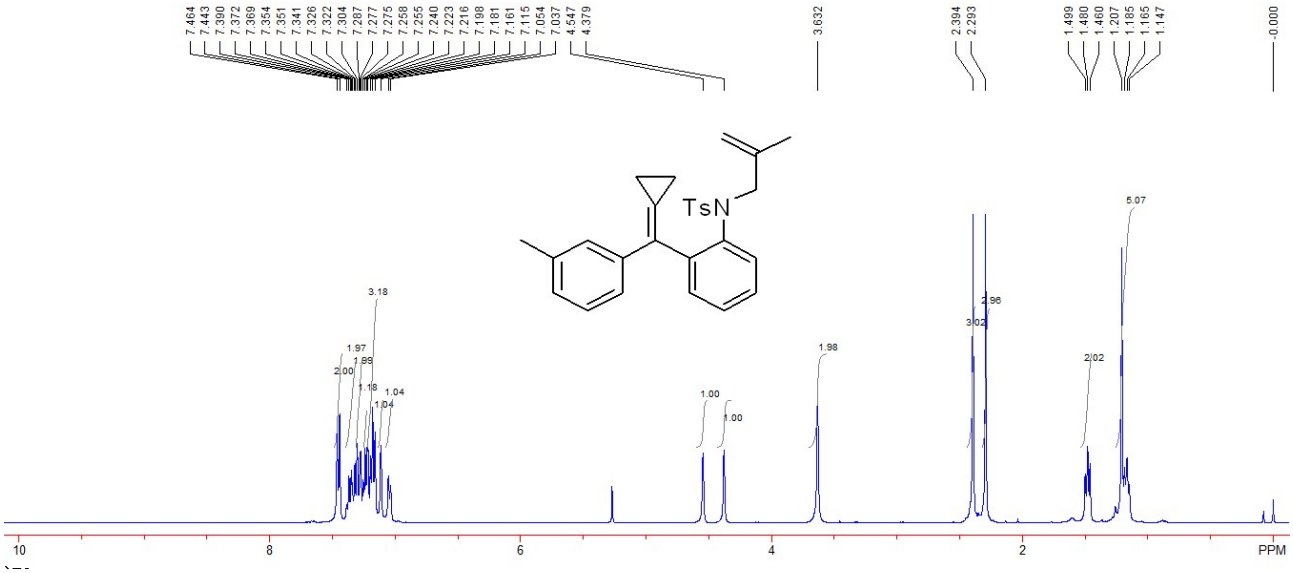


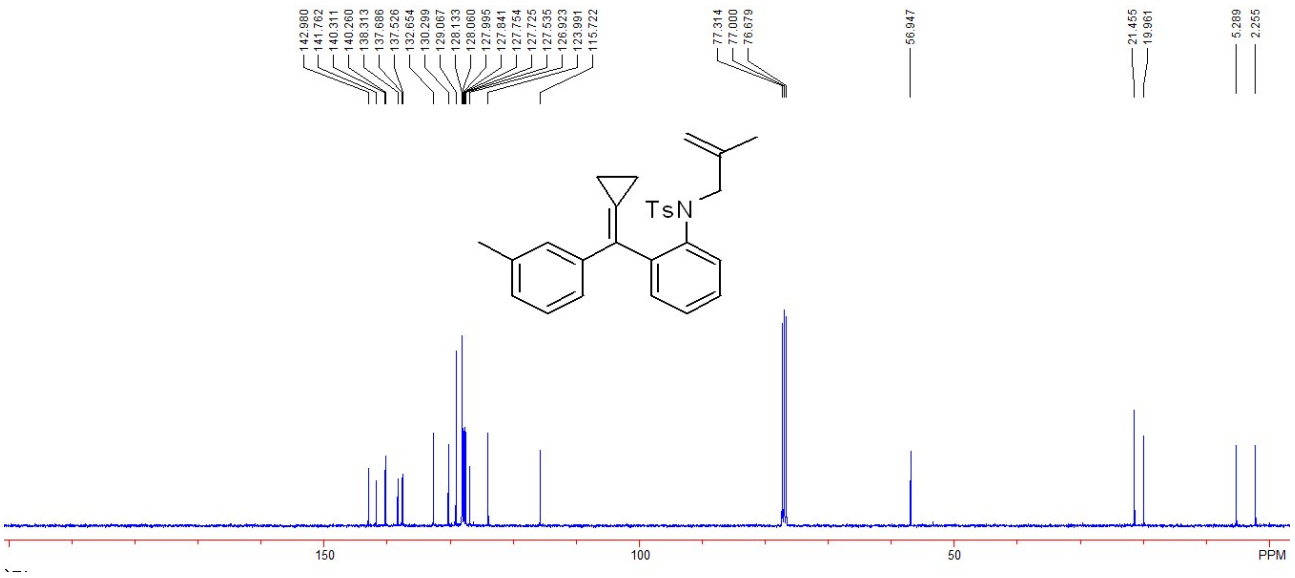



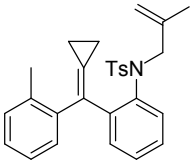





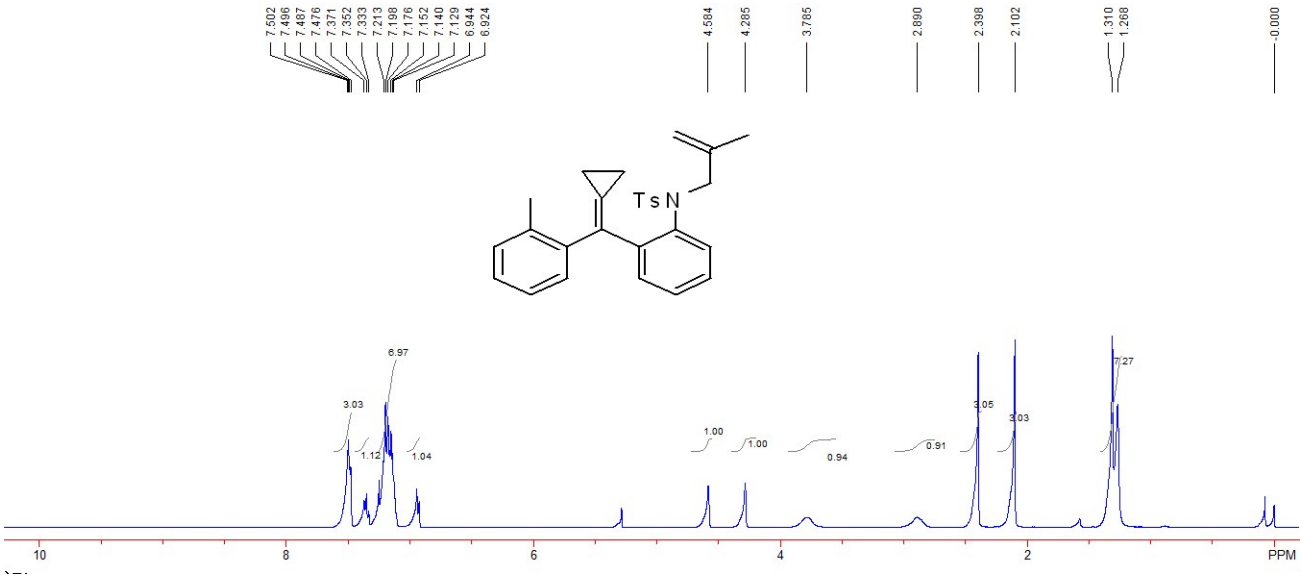

**Compound 1n**: 718 mg, 81%, A white solid, m.p. 124-126 $^{o}$C; IR ($CH_2Cl_2$): ν 3030, 2927, 2921, 1599, 1485, 1443, 1341, 1157, 1092, 1020, 903, 883, 868, 815, 786, 669, 654 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (t, 2H, *J* = 7.6 Hz), 1.21 (s, 3H), 1.48 (t, 2H, *J* = 7.6 Hz), 2.29 (s, 3H), 2.39 (s, 3H), 3.63 (s, 2H), 4.38 (s, 1H), 4.55 (s, 1H), 7.05 (d, 1H, *J* = 6.8 Hz), 7.12 (s, 1H), 7.16-7.22 (m, 3H), 7.24-7.26 (m, 1H), 7.28-7.30 (m, 2H), 7.32-7.37 (m, 2H), 7.45 (d, 2H, *J* = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.3, 20.0, 21.5, 56.9, 115.7, 124.0, 126.9, 127.5, 127.7, 127.75, 127.84, 128.0, 128.06, 128.13, 129.1, 130.3, 132.7, 137.5, 137.7, 138.3, 140.26, 140.31, 141.8, 143.0; MS (ESI) *m/z*: 444.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{30}NO_2S^+$ requires: 444.1992, Found: 444.1993.

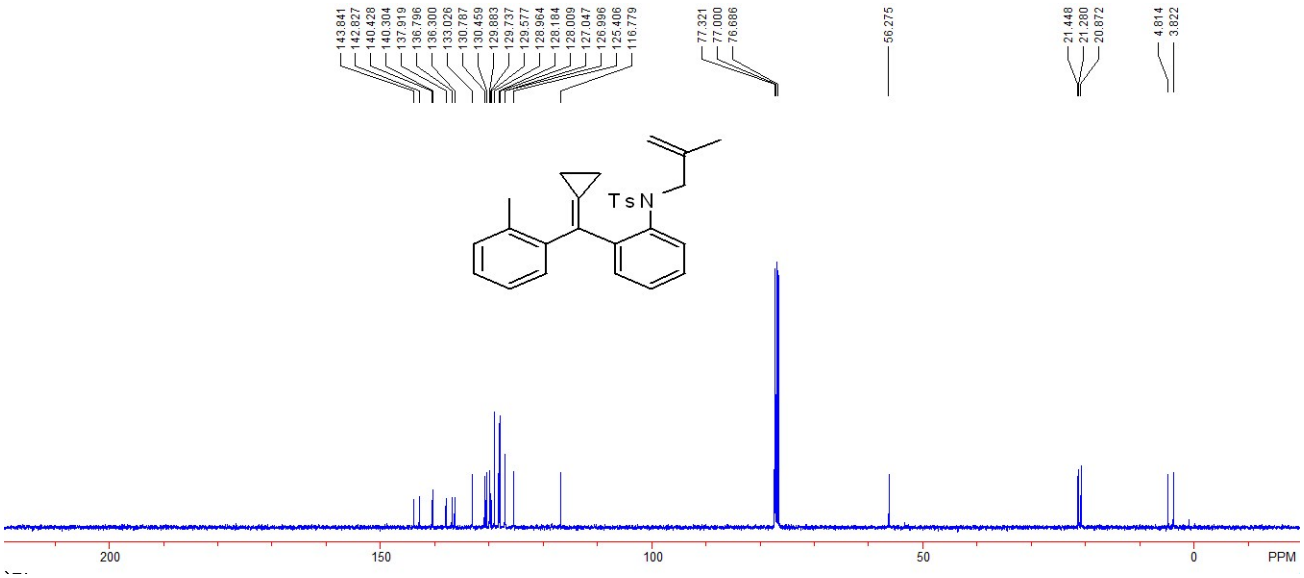


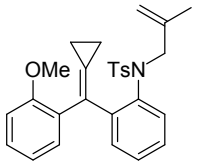


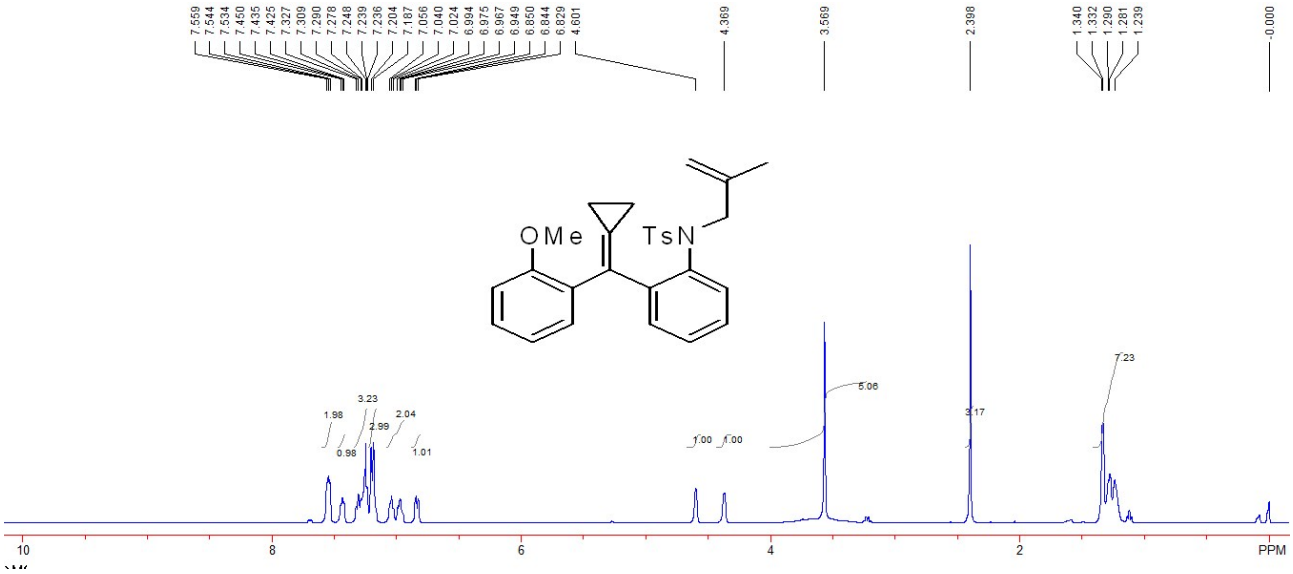

**Compound 1o**: 762 mg, 86%, A white solid, m.p. 136-138 $^{o}$C; IR ($CH_2Cl_2$): ν 3061, 2974, 2923, 1597, 1485, 1443, 1344, 1161, 1093, 1024, 908, 861, 815, 761, 654 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27 (s, 4H), 1.31 (s, 3H), 2.10 (s, 3H), 2.40 (s, 3H), 2.89 (s, 1H), 3.79 (s, 1H), 4.29 (s, 1H), 4.58 (s, 1H), 6.93 (d, 1H, *J* = 8.0 Hz), 7.13-7.21 (m, 7H), 7.35 (t, 1H, *J* = 7.6 Hz), 7.48-7.50 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 3.8, 4.8, 20.9, 21.3, 21.4, 56.3, 116.8, 125.4, 127.00, 127.05, 128.0, 128.2, 129.0, 129.6, 129.7, 129.9, 130.5, 130.8, 133.0, 136.3, 136.8, 137.9, 140.3, 140.4, 142.8, 143.8; MS (ESI) *m/z*: 461.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{33}N_2O_2S^+$ requires: 461.2257, Found: 461.2257.

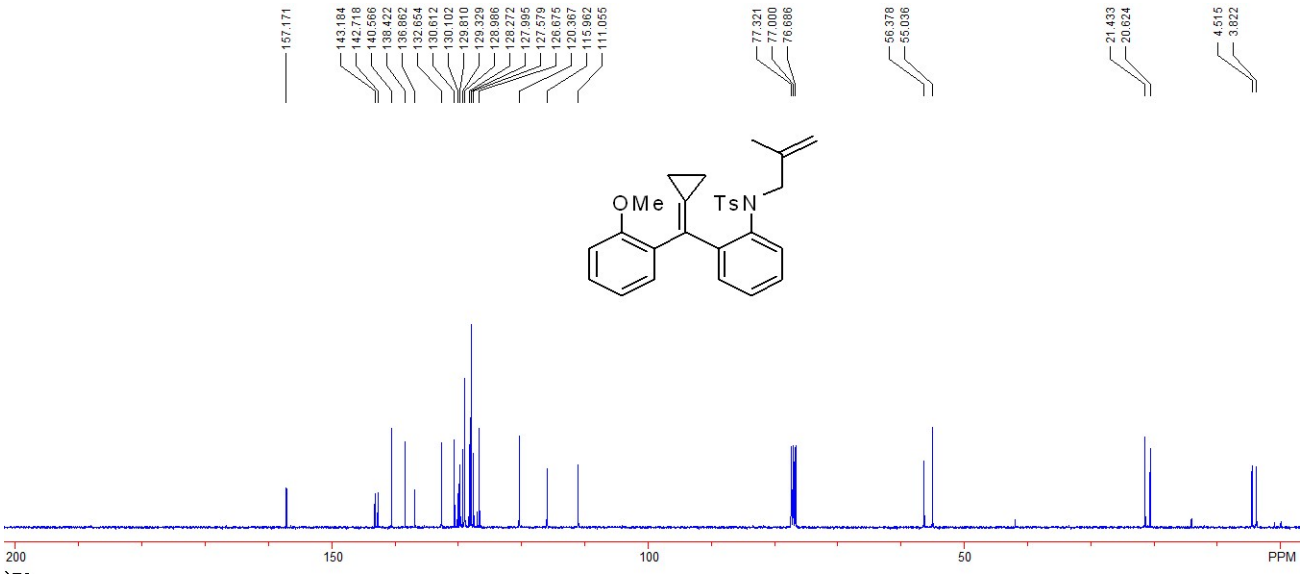


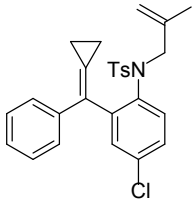


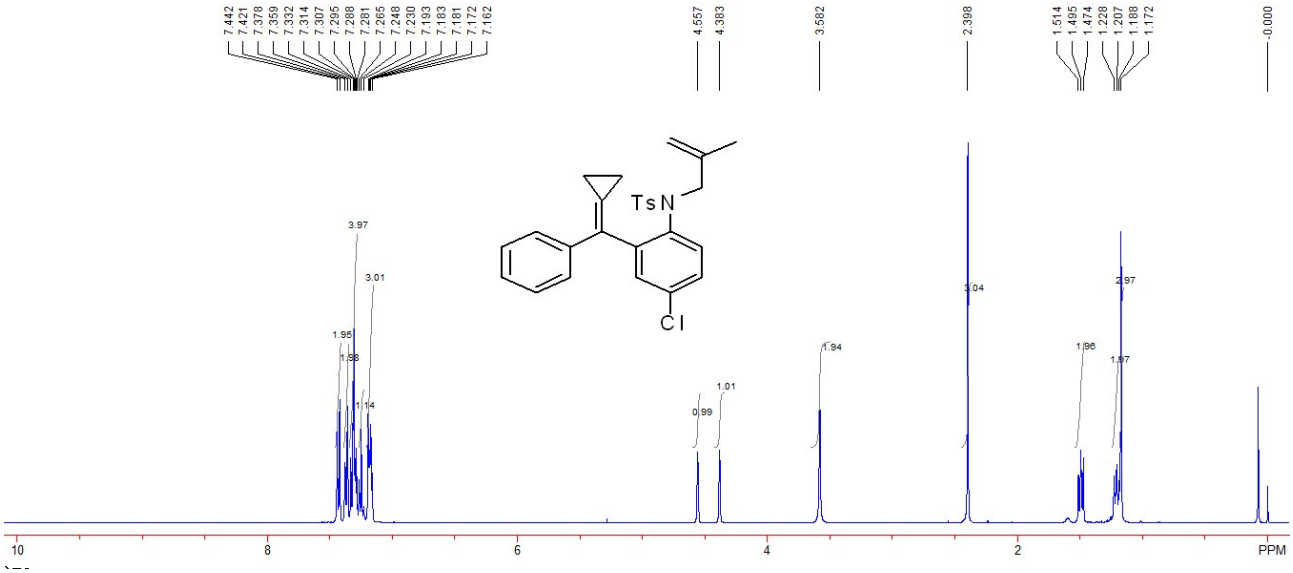

**Compound 1p**: 827 mg, 90%, A white solid, m.p. 141-143 $^{o}$C; IR ($CH_2Cl_2$): ν 2974, 2923, 2831, 1597, 1490, 1456, 1341, 1245, 1158, 1092, 1045, 1027, 880, 816, 755, 697, 653 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24-1.34 (m, 7H), 2.40 (s, 3H), 3.57 (brs, 5H), 4.37 (s, 1H), 4.60 (s, 1H), 6.84 (dd, 1H, $J_1$ = 8.4 Hz, $J_2$ = 2.4 Hz), 6.95-7.06 (m, 2H), 7.19-7.20 (m, 3H), 7.24-7.33 (m, 3H), 7.43-7.45 (m, 1H), 7.53-7.56 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 3.8, 4.5, 20.6, 21.4, 55.0, 56.4, 111.1, 116.0, 120.4, 126.7, 127.6, 128.0, 128.3, 129.0, 129.3, 129.8, 130.1, 130.6, 132.7, 136.9, 138.4, 140.6, 142.7, 143.2, 157.2; MS (ESI) *m/z*: 477.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{33}N_2O_3S^+$ requires: 477.2206, Found: 477.2207.

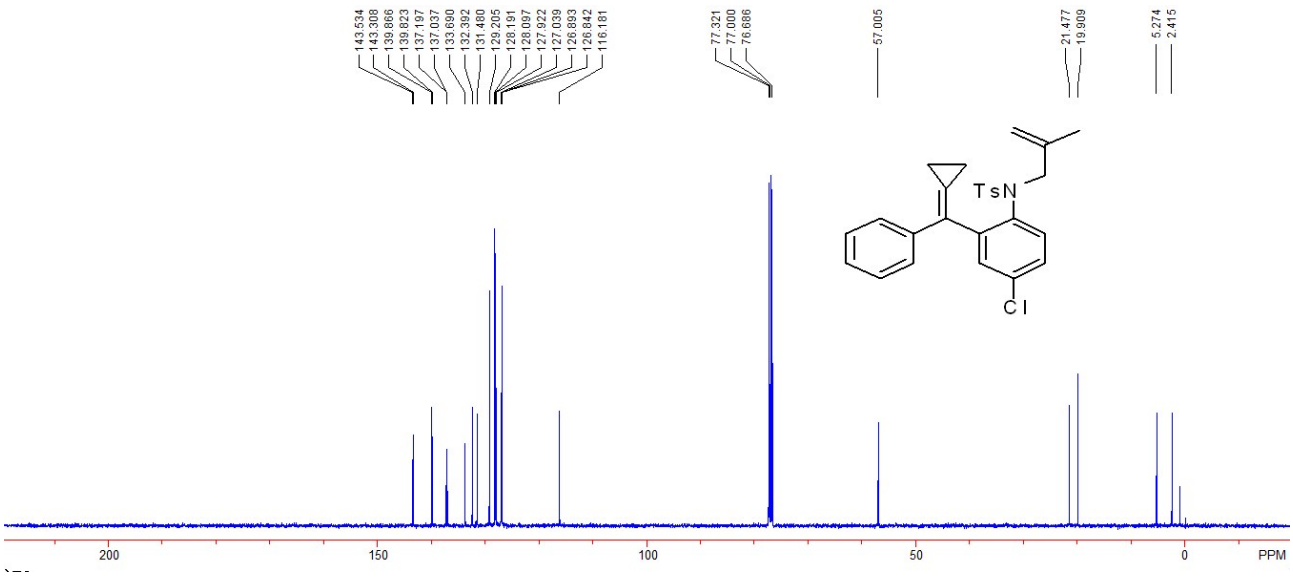


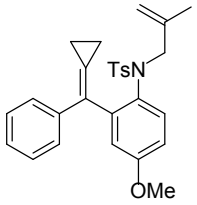


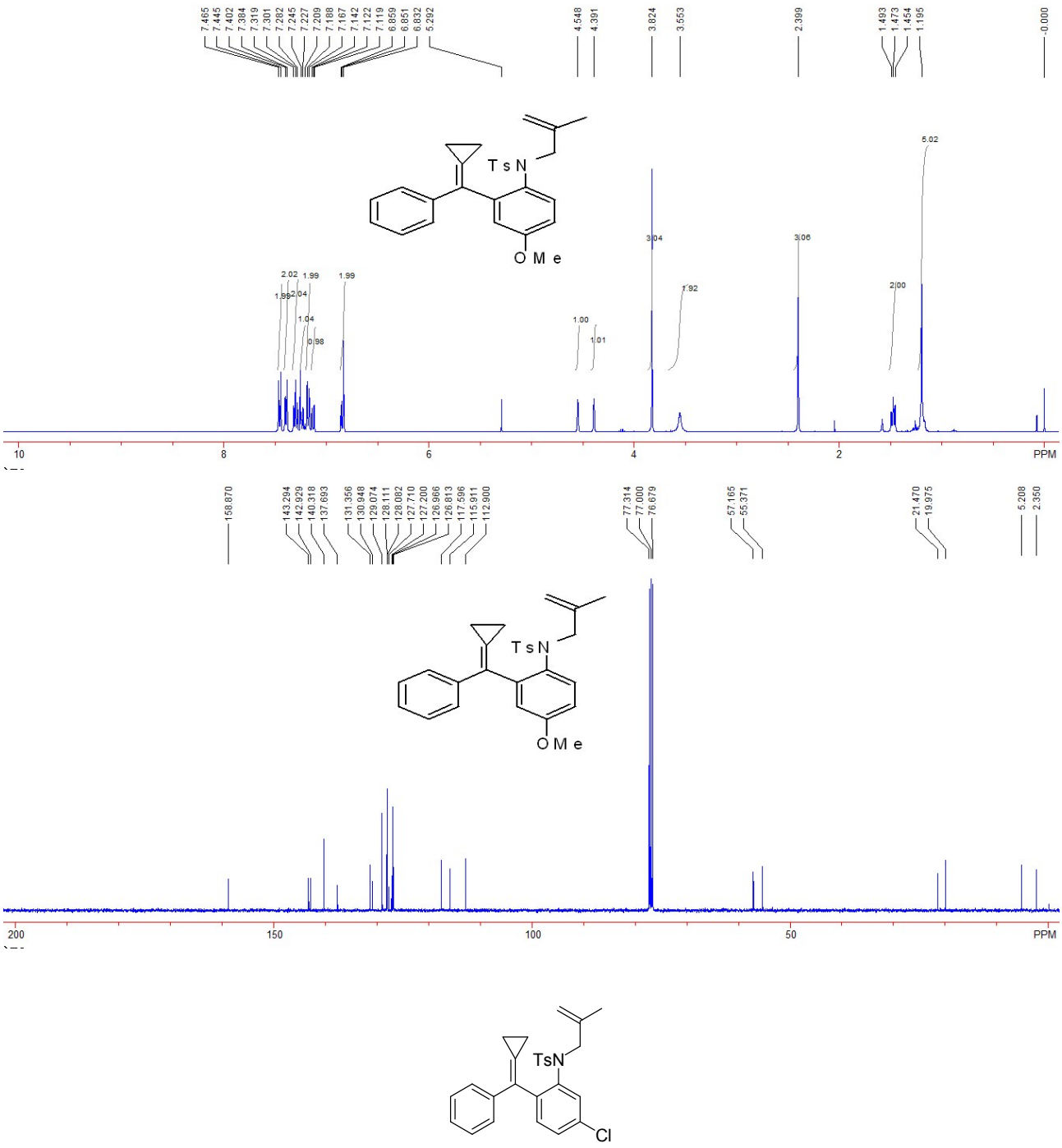

**Compound 1q**: 741 mg, 80%, A white solid, m.p. 134-136 $^{o}$C; IR ($CH_2Cl_2$): ν 2974, 2925, 2881, 1494, 1480, 1341, 1159, 1091, 1045, 879, 815, 775, 741, 664 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (s, 3H), 1.21 (t, 2H, *J* = 8.0 Hz), 1.50 (t, 2H, *J* = 8.0 Hz), 2.40 (s, 3H), 3.58 (s, 2H), 4.38 (s, 1H), 4.56 (s, 1H), 7.16-7.19 (m, 3H), 7.23-7.27 (m, 1H), 7.28-7.33 (m, 4H), 7.37 (d, 2H, *J* = 7.6 Hz), 7.43 (d, 2H, *J* = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.4, 5.3, 19.9, 21.5, 57.0, 116.2, 126.8, 126.9, 127.0, 127.9, 128.1, 128.2, 129.2, 131.5, 132.4, 133.7, 137.0, 137.2, 139.8, 139.9, 143.3, 143.5; MS (ESI) *m/z*: 481.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{30}ClN_2O_2S^+$ requires: 481.1711, Found: 481.1712.





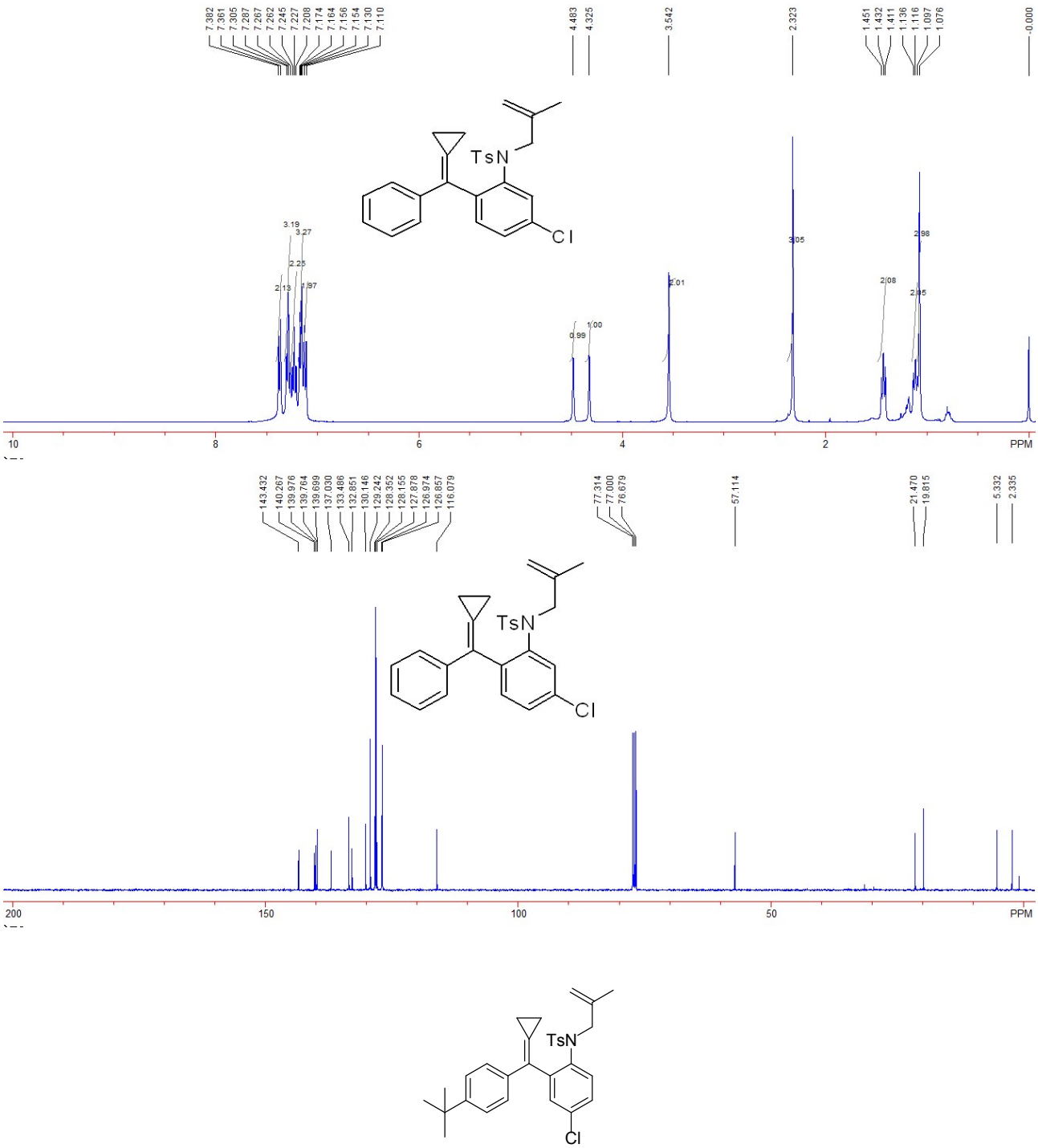

**Compound 1r**: 781 mg, 85%, A white solid, m.p. 105-107 $^{o}$C; IR ($CH_2Cl_2$): ν 3059, 2972, 2834, 1598, 1571, 1493, 1445, 1327, 1302, 1208, 1158, 1092, 1033, 866, 815, 696, 679 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17-1.20 (m, 5H), 1.47 (t, 2H, $J$ = 7.6 Hz), 2.40 (s, 3H), 3.55 (s, 2H), 3.82 (s, 3H), 4.39 (s, 1H), 4.55 (s, 1H), 6.83-6.85 (m, 2H), 7.12 (dd, 1H, $J_1$ = 8.4 Hz, $J_2$ = 1.6 Hz), 7.18 (d, 2H, $J$ = 8.4 Hz), 7.21-7.25 (m, 1H), 7.30 (t, 2H, $J$ = 7.2 Hz), 7.39 (d, 2H, $J$ = 7.2 Hz), 7.46 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.4, 5.2, 20.0, 21.5, 55.4, 57.2, 112.9, 115.9, 117.6, 126.8, 127.0, 127.2, 127.7, 128.08, 128.11, 129.1, 130.9, 131.4, 137.7, 140.3, 142.9, 143.3, 158.9; MS (ESI) *m/z*: 460.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{30}NO_3S^+$ requires: 460.1941, Found: 460.1942.





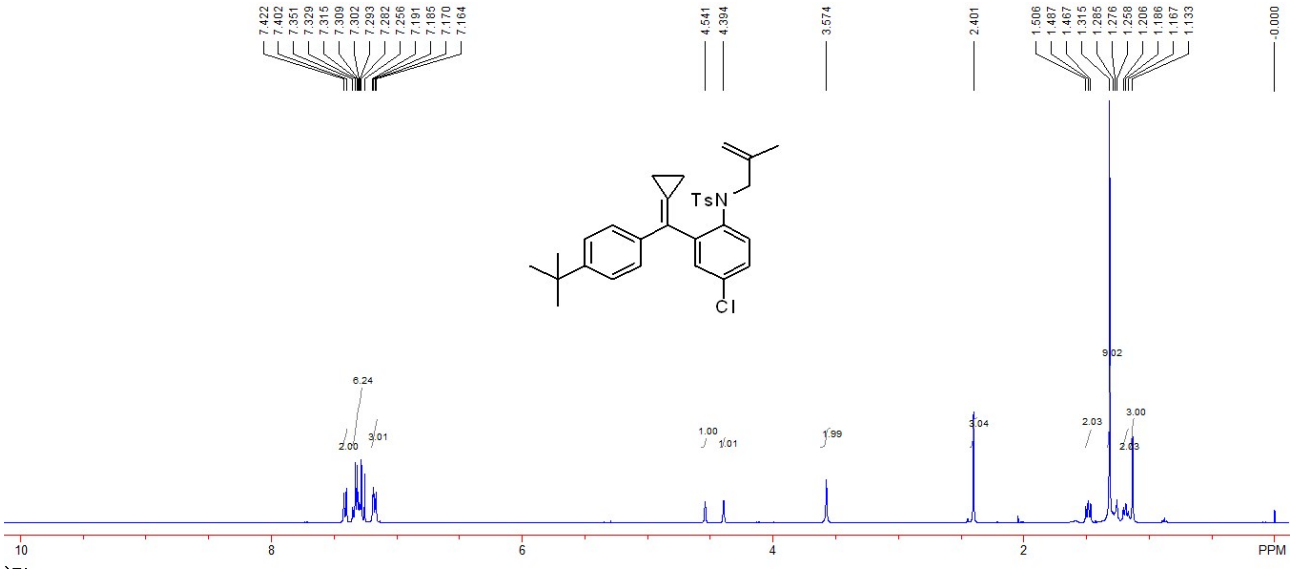


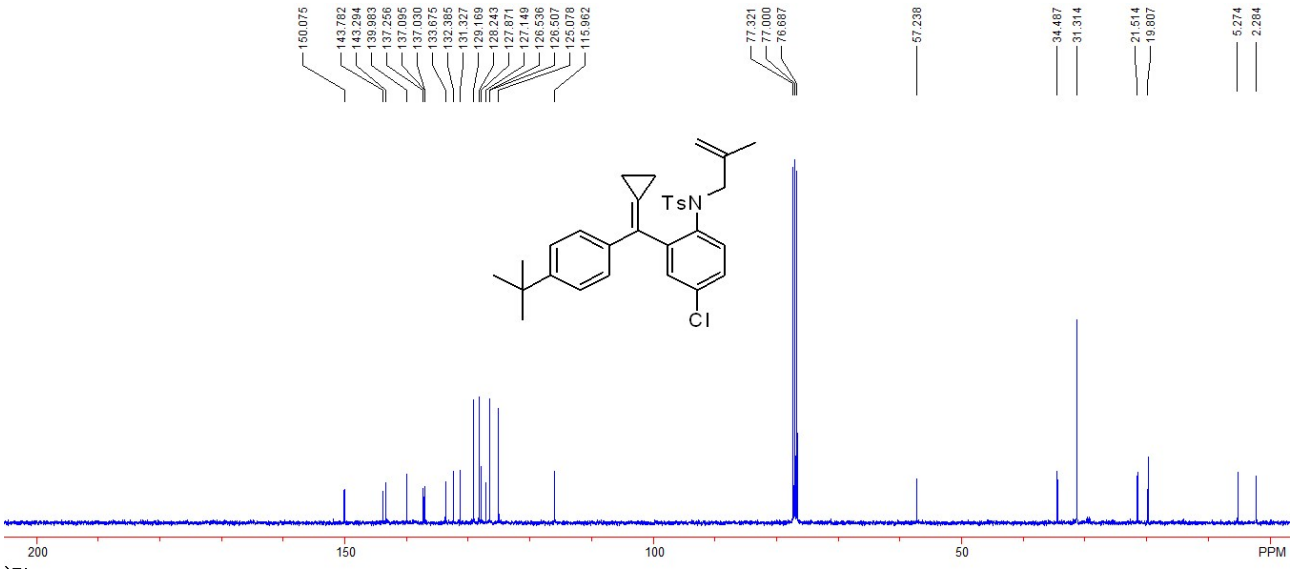
**Compound 1s**: 769 mg, 83%, A white solid, m.p. 135-137 $^{o}$C; IR ($CH_2Cl_2$): ν 2960, 2923, 2855, 1597, 1493, 1446, 1352, 1338, 1260, 1161, 1092, 1028, 909, 843, 815, 698, 678 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.08 (s, 3H), 1.12 (t, 2H, *J* = 7.6 Hz), 1.43 (t, 2H, *J* = 7.6 Hz), 2.32 (s, 3H), 3.54 (s, 2H), 4.33 (s, 1H), 4.48 (s, 1H), 7.12 (d, 2H, *J* = 8.0 Hz), 7.15-7.17 (m, 3H), 7.23 (t, 2H, *J* = 7.6 Hz), 7.26-7.31 (m, 3H), 7.37 (d, 2H, *J* = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.3, 19.8, 21.5, 57.1, 116.1, 126.9, 127.0, 127.9, 128.2, 128.4, 129.2, 130.1, 132.9, 133.5, 137.0, 139.7, 139.8, 140.0, 140.3, 143.4; MS (ESI) *m/z*: 481.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{30}ClN_2O_2S^+$ requires: 481.1711, Found: 481.1714.

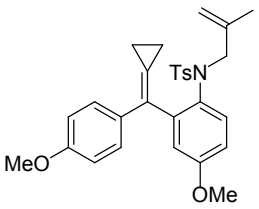



**Compound 1t**: 893 mg, 86%, A white solid, m.p. 143-145 $^{o}$C; IR ($CH_2Cl_2$): ν 2964, 2904, 2868, 1598, 1510, 1482, 1343, 1185, 1159, 1091, 1022, 864, 815, 710, 671 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.13 (s, 3H), 1.19 (t, 2H, $J$ = 7.6 Hz), 1.32 (s, 9H), 1.49 (t, 2H, $J$ = 7.6 Hz), 2.40 (s, 3H), 3.57 (s, 2H), 4.39 (s, 1H), 4.54 (s, 1H), 7.16-7.19 (m, 3H), 7.28-7.35 (m, 6H), 7.41 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.3, 19.8, 21.5, 31.3, 34.5, 57.2, 116.0, 125.1, 126.51, 126.54, 127.1, 127.9, 128.2, 129.2, 131.3, 132.4, 133.7, 137.0, 137.1, 137.3, 140.0, 143.3,

143.8, 150.1; MS (ESI) *m/z*: 537.2 (M+$NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{38}ClN_2O_2S^+$ requires: 537.2337, Found: 537.2338.

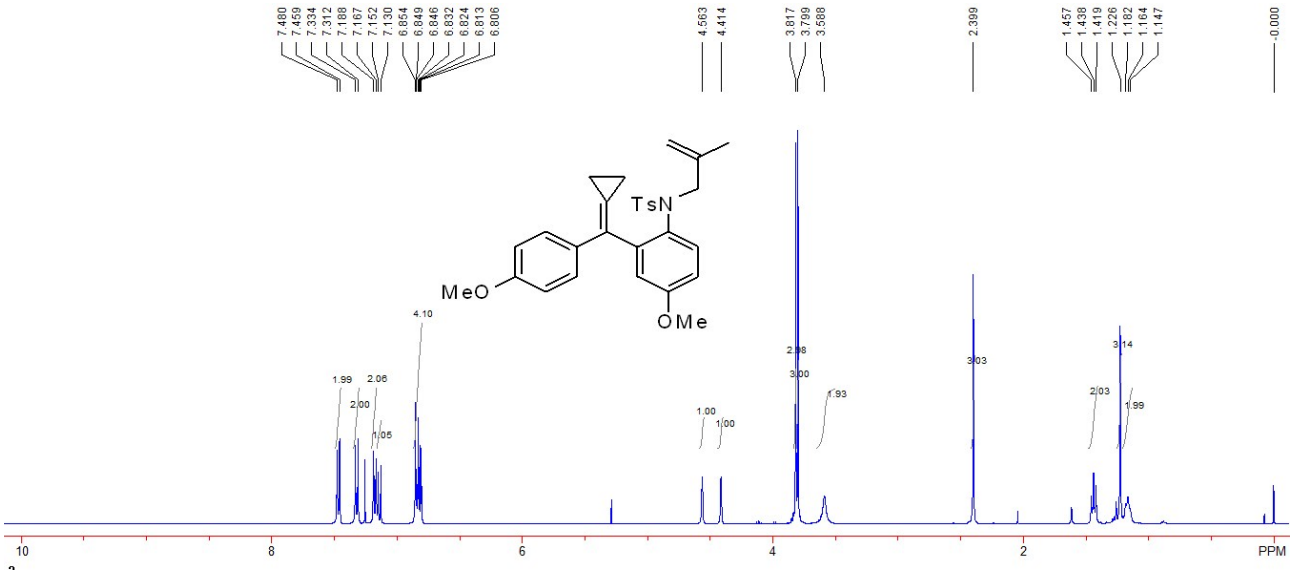


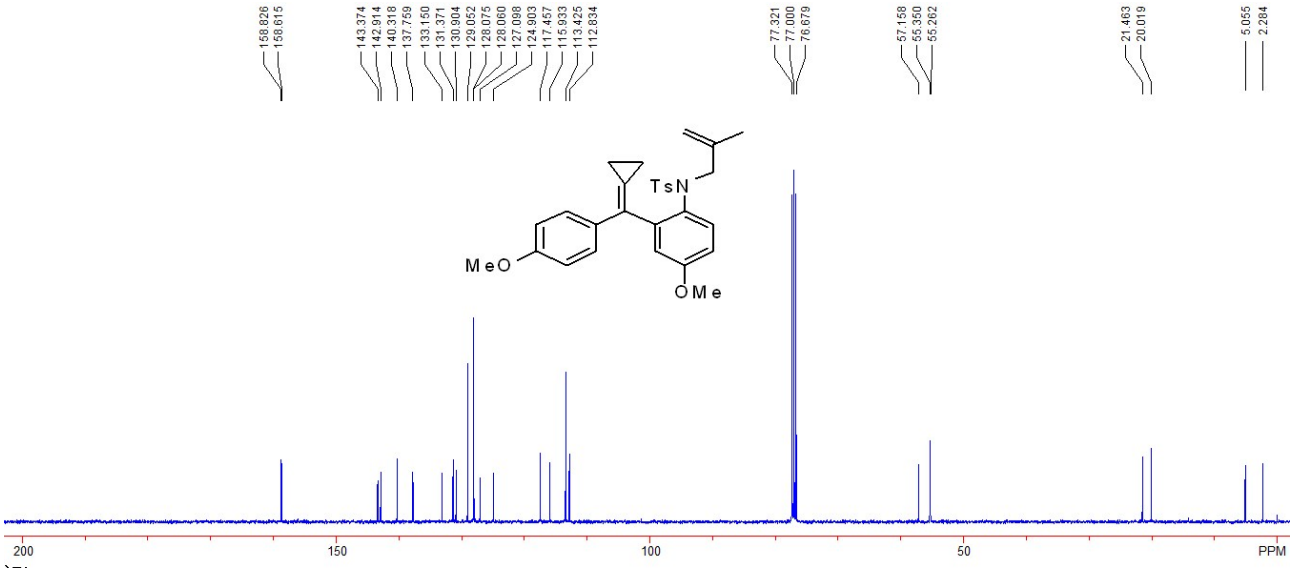



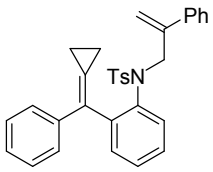




**Compound 1u**: 802 mg, 82%, A white solid, m.p. 85-87 $^oC$; IR ($CH_2Cl_2$): ν 2971, 2934, 2836, 1604, 1572, 1509, 1493, 1463, 1340, 1300, 1247, 1159, 1092, 1034, 865, 834, 815, 680 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.16 (t, 2H, *J* = 7.6 Hz), 1.23 (s, 3H), 1.44 (t, 2H, *J* = 7.6 Hz), 2.40 (s, 3H), 3.59 (s, 2H), 3.80 (s, 3H), 3.82 (s, 3H), 4.41 (s, 1H), 4.56 (s, 1H), 6.81-6.83 (m, 1H), 6.85-6.86 (m, 3H), 7.13(s, 1H), 7.15-7.19 (m, 2H), 7.32 (d, 2H, *J* = 8.8 Hz), 7.47 (d, 2H, *J* = 8.4

Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 5.1, 20.0, 21.5, 55.3, 55.4, 57.2, 112.8, 113.4, 115.9, 117.5, 124.9, 127.1, 128.06, 128.08, 129.1, 130.9, 131.4, 133.2, 137.8, 140.3, 142.9, 143.4, 158.6, 158.8; MS (ESI) *m/z*: 490.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{29}H_{32}NO_4S^+$ requires: 490.2047, Found: 490.2045.

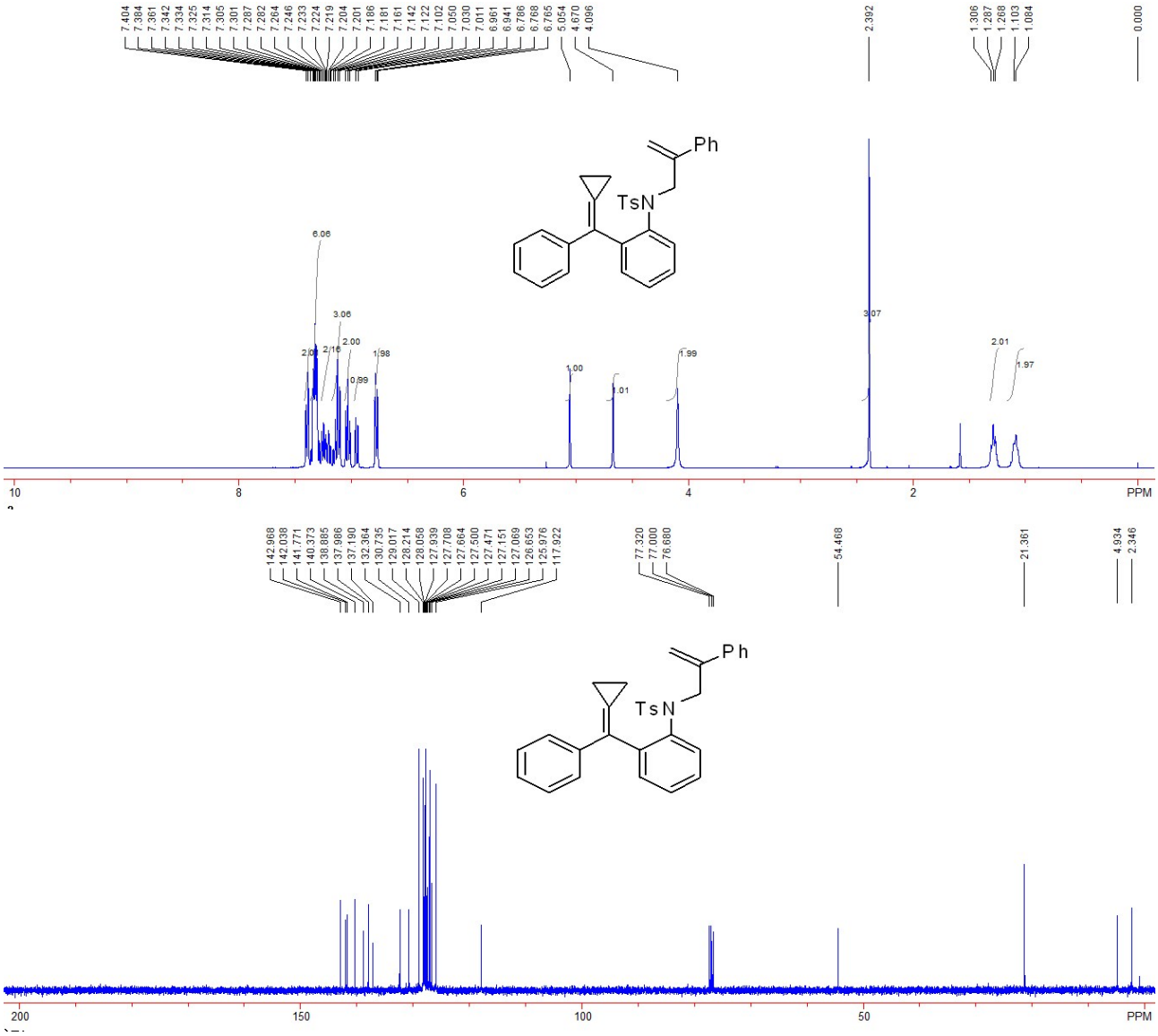


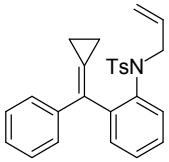




**Compound 1v**: 550 mg, 56%, A white solid, m.p. 135-137 $^oC$; IR ($CH_2Cl_2$): ν 3059, 2975, 2929, 1597, 1493, 1446, 1335, 1155, 1090, 1020, 924, 815, 766, 697, 661 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.08 (t, 2H, $J$ = 7.6 Hz), 1.29 (t, 2H, $J$ = 7.6 Hz), 2.39 (s, 3H), 4.10 (s, 2H), 4.67 (s, 1H), 5.05 (s, 1H), 6.78 (dd, 2H, $J_1$ = 8.4 Hz, $J_2$ = 1.2 Hz), 6.95 (d, 1H, $J$ = 8.0 Hz), 7.03 (t, 2H, $J$ =

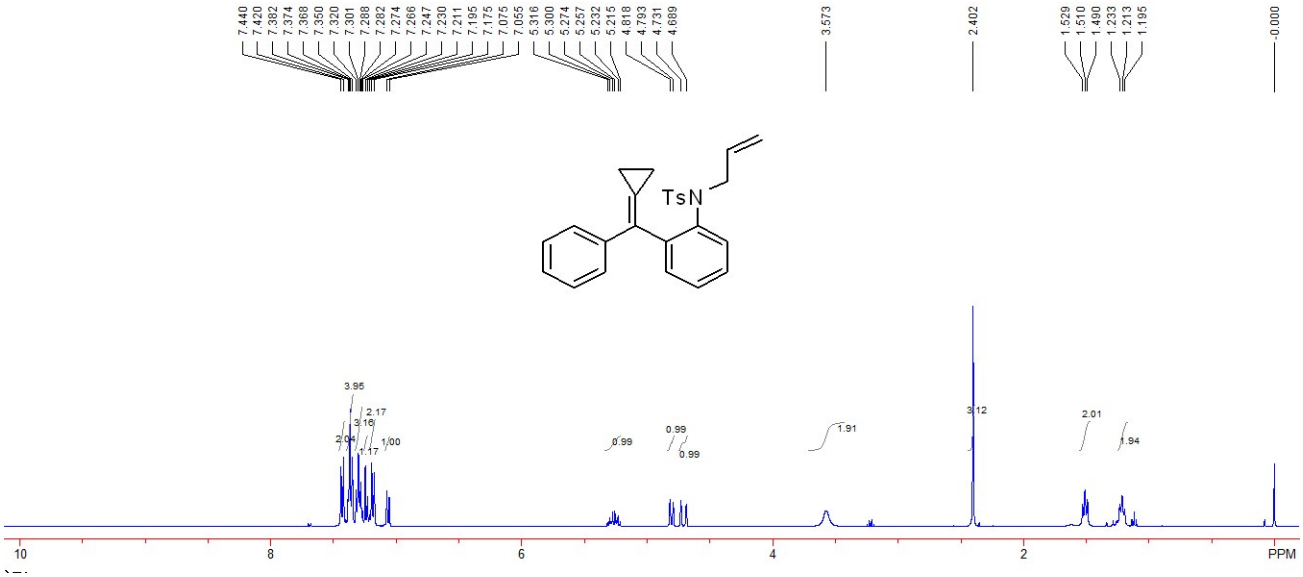
8.0 Hz), 7.10-7.16 (m, 3H), 7.18-7.26(m, 2H), 7.28-7.36 (m, 6H), 7.39 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 4.9, 21.4, 54.5, 117.9, 126.0, 126.7, 127.1, 127.2, 127.47, 127.50, 127.66, 127.71, 127.9, 128.1, 128.2, 129.0, 130.7, 132.4, 137.2, 138.0, 138.9, 140.4, 141.8, 142.0, 143.0; MS (ESI) *m/z*: 509.2 (M+$NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{32}H_{33}N_2O_2S^+$ requires: 509.2257, Found: 509.2257.

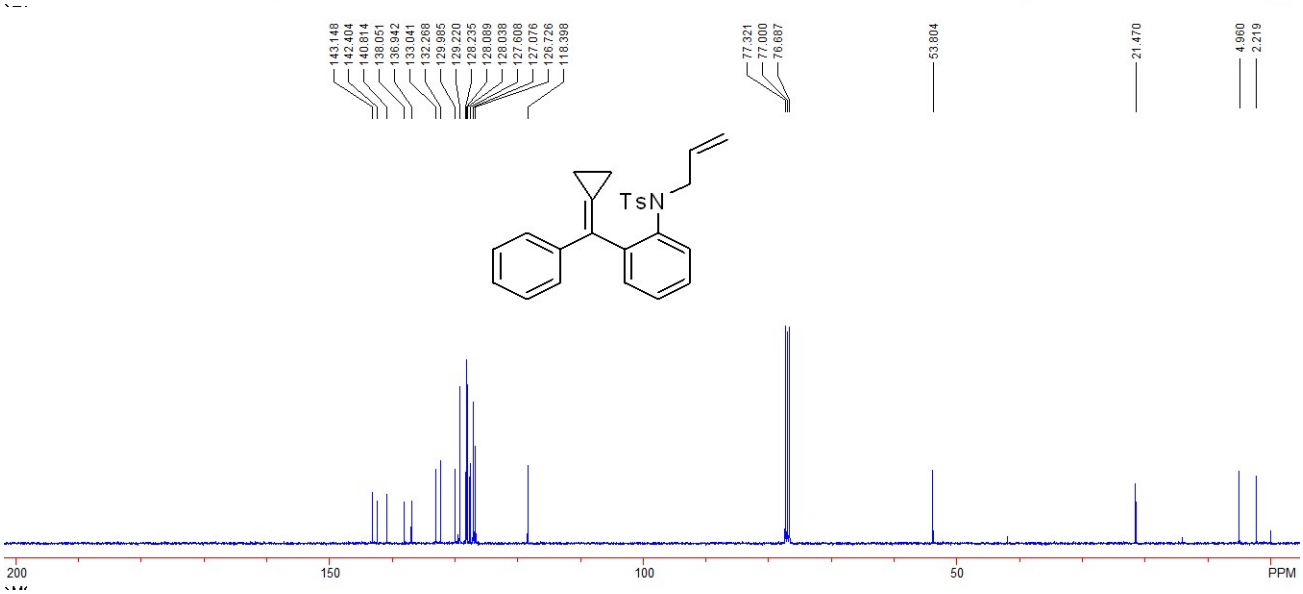


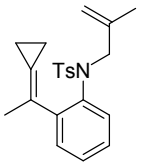




**Compound 1w**: 614 mg, 74%, A white solid, m.p. 106-108 $^{o}$C; IR ($CH_2Cl_2$): ν 3055, 2975, 2920, 1597, 1494, 1445, 1351, 1163, 1091, 856, 816, 767, 697, 663 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.21 (t, 2H, $J$ = 7.6 Hz), 1.51 (t, 2H, $J$ = 7.6 Hz), 2.40 (s, 3H), 3.57 (s, 2H), 4.71 (d, 1H, $J$

= 16.8 Hz), 4.81 (d, 1H, *J* = 10.0 Hz), 5.22-5.32 (m, 1H), 7.07 (d, 1H, *J* = 8.0 Hz), 7.19 (d, 2H, *J* = 8.0 Hz), 7.22 (d, 1H, *J* = 7.6 Hz), 7.25-7.35 (m, 3H), 7.37-7.38 (m, 4H), 7.43 (d, 2H, *J* = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 5.0, 21.5, 53.8, 118.4, 126.7, 127.1, 127.6, 128.0, 128.1, 128.2, 129.2, 130.0, 132.3, 133.0, 136.9, 138.1, 140.8, 142.4, 143.1; MS (ESI) *m/z*: 416.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{26}NO_2S^+$ requires: 416.1679, Found: 416.1680.

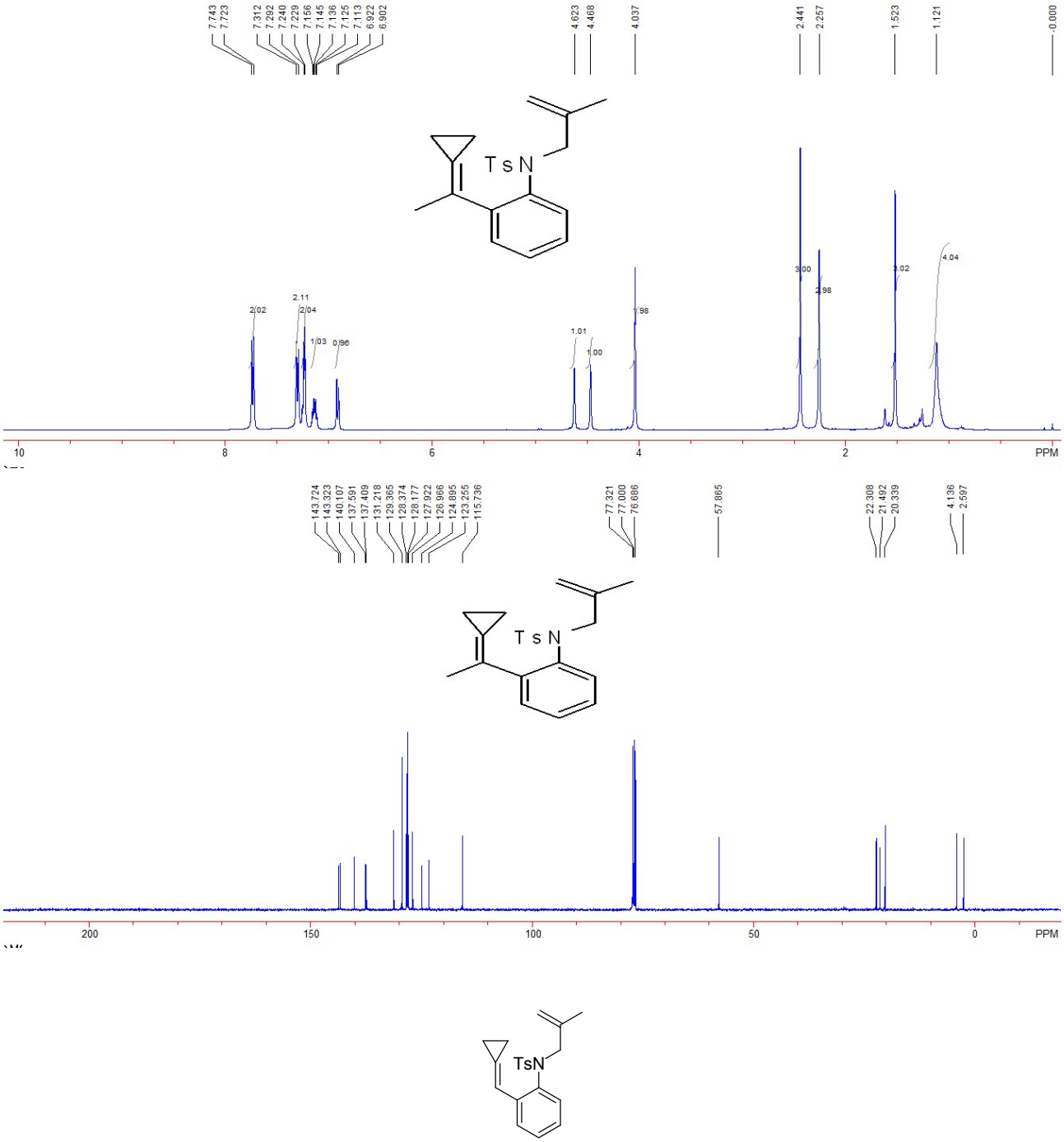



**Compound 1x**: 595 mg, 81%, A white solid, m.p. 100-102 °C; IR ($CH_2Cl_2$): ν 2973, 2921, 2854, 1597, 1484, 1345, 1159, 1092, 1024, 902, 880, 815, 757, 694, 658 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.12 (brs, 4H), 1.52 (s, 3H), 2.26 (s, 3H), 2.44 (s, 3H), 4.04 (s, 2H), 4.47 (s, 1H),

4.62 (s, 1H), 6.91 (d, 1H, $J$ = 8.0 Hz), 7.11-7.16 (m, 1H), 7.23-7.24 (m, 2H), 7.30 (d, 2H, $J$ = 8.0 Hz), 7.73 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.6, 4.1, 20.3, 21.5, 22.3, 57.9, 115.7, 123.3, 124.9, 127.0, 127.9, 128.2, 128.4, 129.4, 131.2, 137.4, 137.6, 140.1, 143.3, 143.7; MS (ESI) *m/z*: 368.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{22}H_{26}NO_2S^+$ requires: 368.1679, Found: 368.1679.

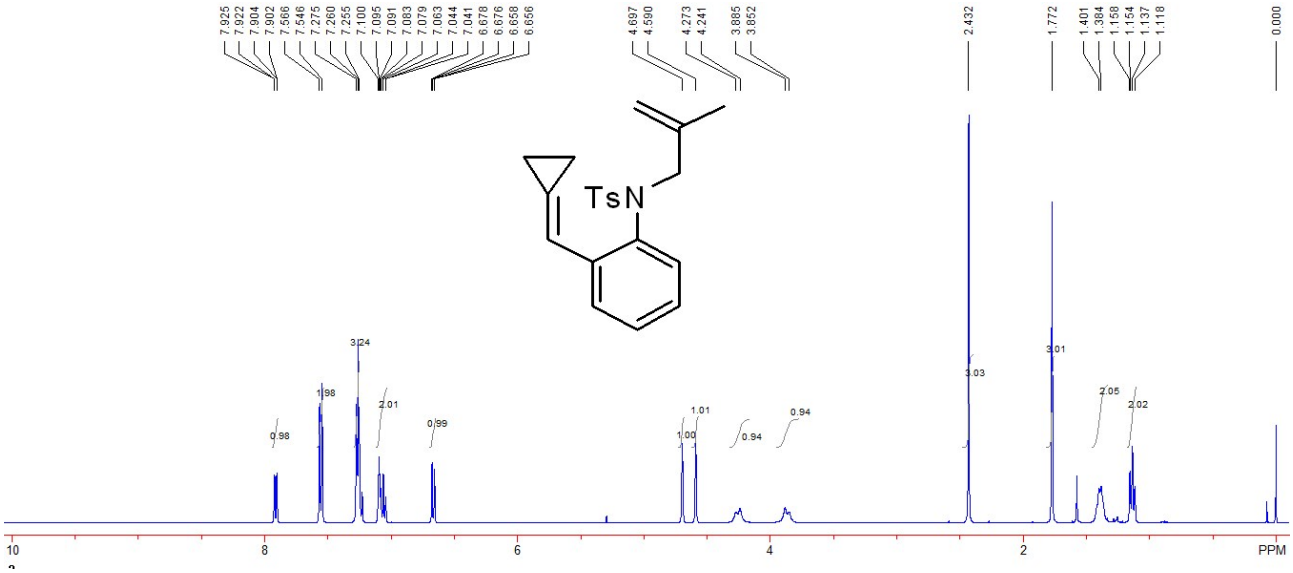


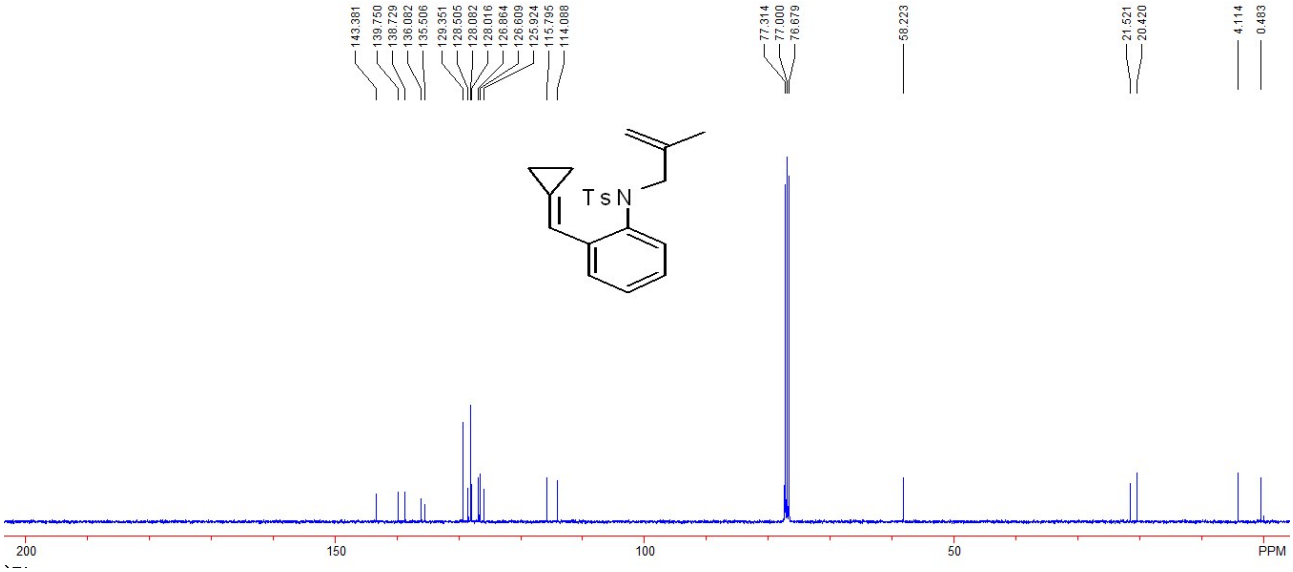


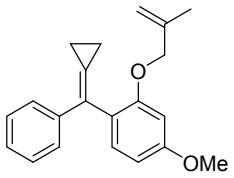


**Compound 1y**: 544 mg, 77%, A white solid, m.p. 135-137 °C; IR ($CH_2Cl_2$): ν 3070, 2975, 2915, 1597, 1485, 1449, 1346, 1163, 1093, 1026, 865, 815, 771, 692, 656 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.12-1.16 (m, 2H), 1.38-1.40 (m, 2H), 1.77 (s, 3H), 2.43 (s, 3H), 3.87 (d, 1H, $J$ =

13.2 Hz), 4.26 (d, 1H, $J$ = 13.2 Hz), 4.59 (s, 1H), 4.70 (s, 1H), 6.67 (dd, 1H, $J_1$ = 8.0 Hz, $J_2$ = 0.8 Hz), 7.04-7.10 (m, 2H), 7.23-7.28 (m, 3H), 7.56 (d, 2H, $J$ = 8.0 Hz), 7.91 (dd, 1H, $J_1$ = 8.0 Hz, $J_2$ = 0.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 0.5, 4.1, 20.4, 21.5, 58.2, 114.1, 115.8, 125.9, 126.6, 126.9, 128.0, 128.1, 128.5, 129.4, 135.5, 136.1, 138.7, 139.8, 143.4; MS (ESI) *m/z*: 354.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{24}NO_2S^+$ requires: 354.1522, Found: 354.1522.

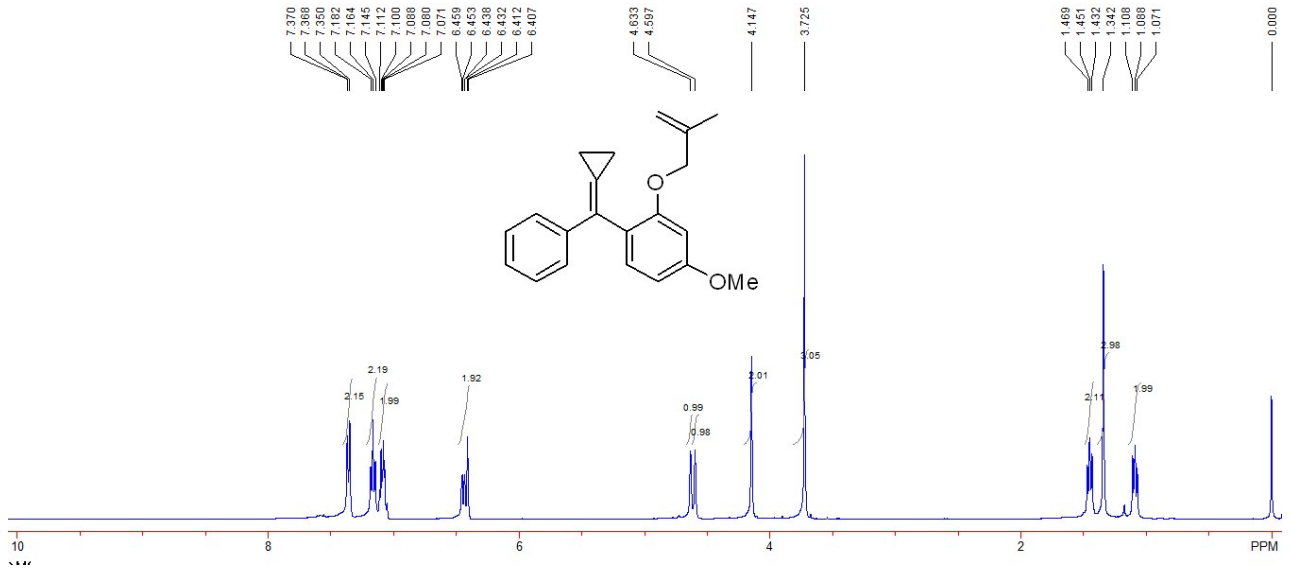


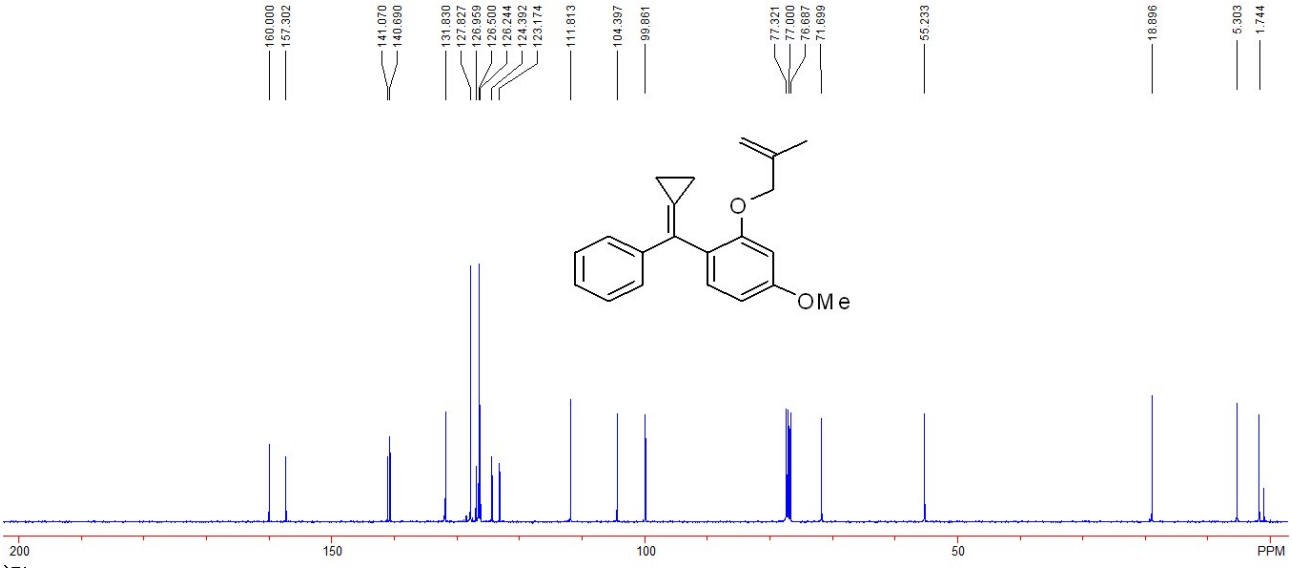



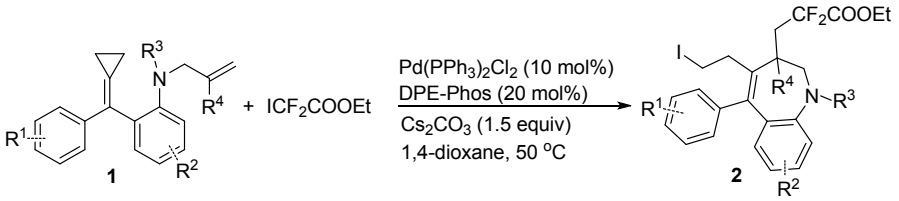

**Compound 1z**: 404 mg, 66%, A white solid, m.p. 128-130 °C; IR ($CH_2Cl_2$): ν 2972, 2931, 2831, 1608, 1578, 1504, 1443, 1305, 1198, 1164, 1088, 1044, 880, 799, 695 $cm^{-1}$; $^1$H NMR (400 MHz,

$CDCl_3$, TMS): δ 1.17-1.11 (m, 2H), 1.34 (s, 3H), 1.43-1.47 (m, 2H), 3.72 (s, 3H), 4.14 (s, 2H), 4.59 (s, 1H), 4.63 (s, 1H), 6.41-6.46 (m, 2H), 7.05-7.11 (m, 2H), 7.16 (t, 2H, *J* = 7.6 Hz), 7.36 (d, 2H, *J* = 7.6 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 1.7, 5.3, 18.9, 55.2, 71.7, 99.9, 104.4, 111.8, 123.2, 124.4, 126.2, 126.5, 127.0, 127.8, 131.8, 140.7, 141.1, 157.3, 160.0; MS (ESI) *m/z*: 307.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{23}O_2^+$ requires: 307.1693, Found: 307.1694.



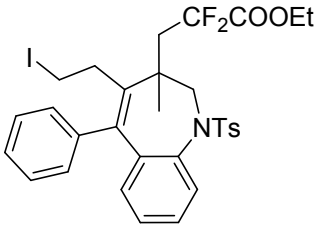



**General procedure for the synthesis of products 2**

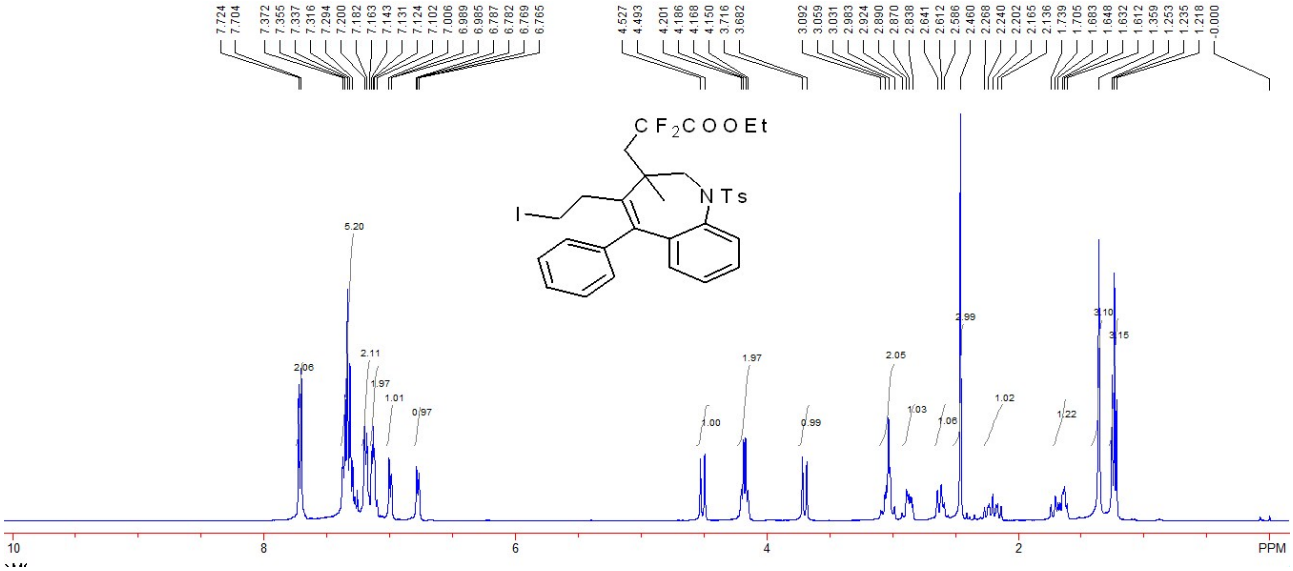


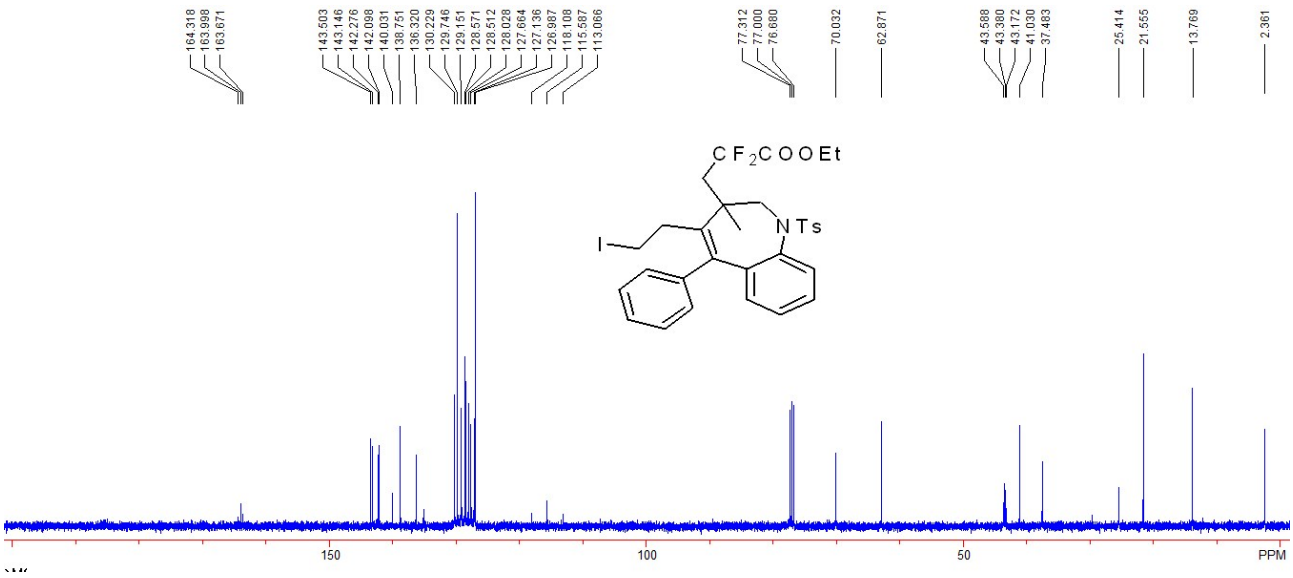

**1** (0.15 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.015 mmol, 0.10 equiv), DPE-Phos (0.030 mmol, 0.20 equiv) and $Cs_2CO_3$ (0.225 mmol, 1.5 equiv) were dissolved in super-dry 1,4-dioxane (1.5 mL), then $ICF_2COOEt$ (0.30 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 50 $^oC$ oil bath. The reaction was stopped after 12 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 8 / 1) to afford the products **2** in good yields.

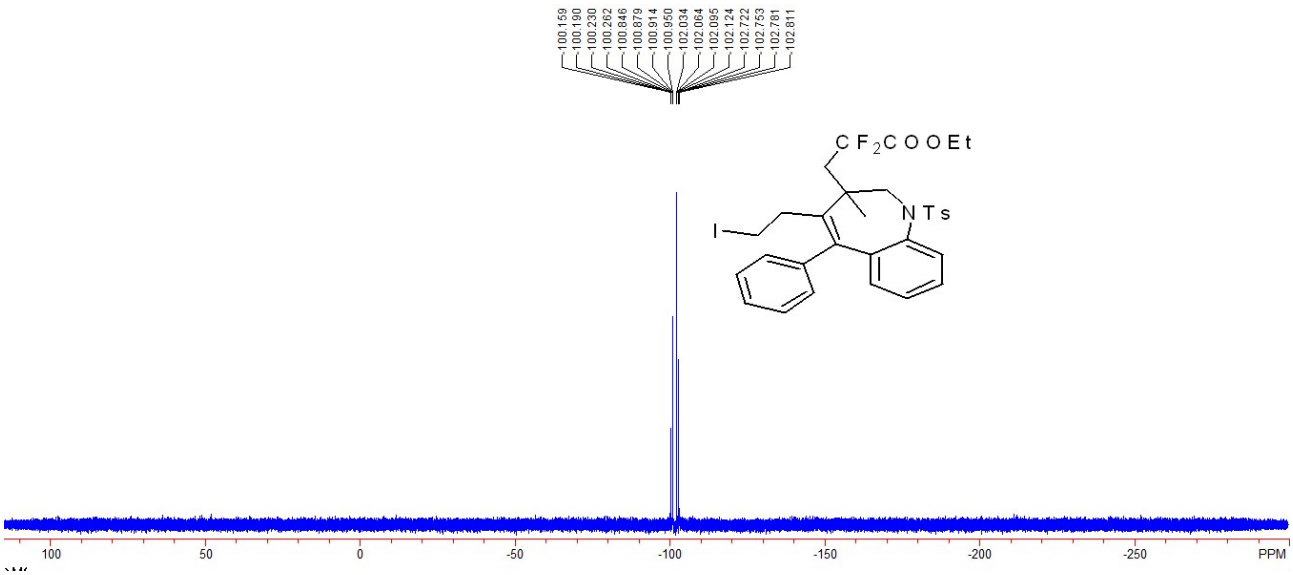
**Spectroscopic data for products 2**

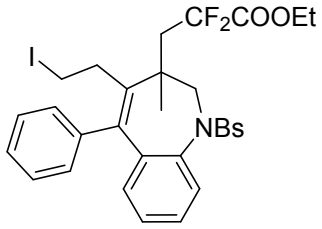



**Compound 2a**: 77 mg, 76%, A white solid, m.p. 130-132 °C; IR ($CH_2Cl_2$): ν 3055, 2981, 2925, 2861, 1765, 1596, 1487, 1343, 1303, 1169, 1156, 1093, 1079, 860, 768, 706 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.36 (s, 3H), 1.61-1.74 (m, 1H), 2.14-2.27 (m, 1H), 2.46 (s, 3H), 2.59-2.64 (m, 1H), 2.84-2.92 (m, 1H), 2.98-3.09 (m, 2H), 3.70 (d, 1H, $J$ = 13.6 Hz), 4.18 (qd, 2H, $J_1$ = 6.8 Hz, $J_2$ = 1.6 Hz), 4.51 (d, 1H, $J$ = 13.6 Hz), 6.78 (dd, 1H, $J_1$ = 7.2 Hz, $J_2$ = 1.6 Hz), 7.00 (dd, 1H, $J_1$ = 7.2 Hz, $J_2$ = 1.6 Hz), 7.10-7.14 (m, 2H), 7.19 (d, 2H, $J$ = 7.2 Hz), 7.29-7.37 (m, 5H), 7.71 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.4, 13.8, 21.6, 25.4, 37.5, 41.0, 43.4 (t, $J_{C\text{-}F}$ = 20.8 Hz), 62.9, 70.0, 115.6 (t, $J_{C\text{-}F}$ = 252.1 Hz), 127.0, 127.1, 127.7, 128.0, 128.5, 128.6, 129.2, 129.7, 130.2, 136.3, 138.8, 140.0, 142.1, 142.3, 143.1, 143.5, 164.0 (t, $J_{C\text{-}F}$ = 32.7 Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.5 (ddd, 1F, $J_1$ = 258.3 Hz, $J_2$ = 26.7 Hz, $J_3$ = 11.7 Hz), -102.4 (ddd, 1F, $J_1$ = 258.3 Hz, $J_2$ = 21.8 Hz, $J_3$ = 11.3 Hz); MS (ESI) *m/z*: 697.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{36}F_2IN_2O_4S^+$ requires: 697.1403, Found: 697.1401.



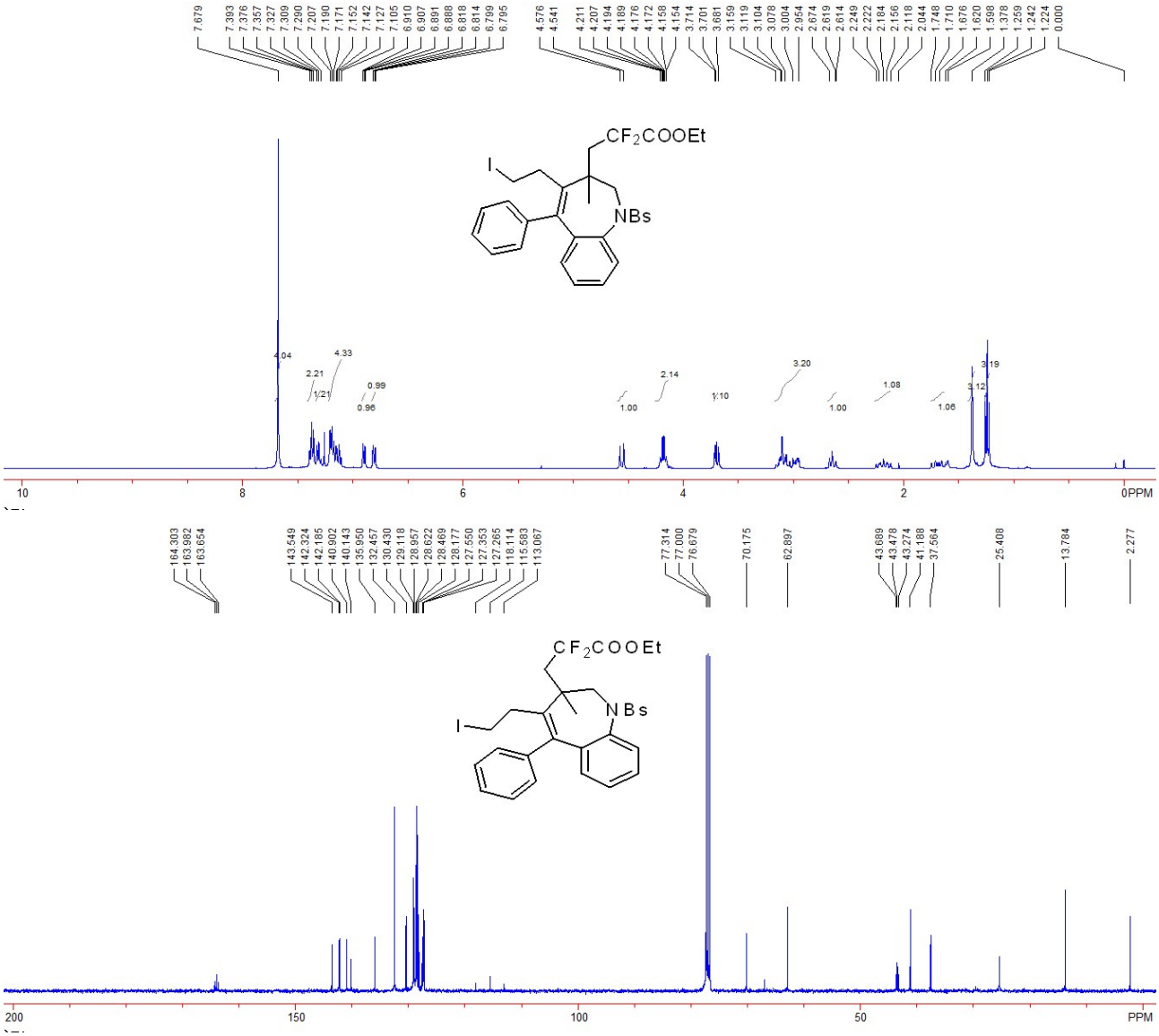


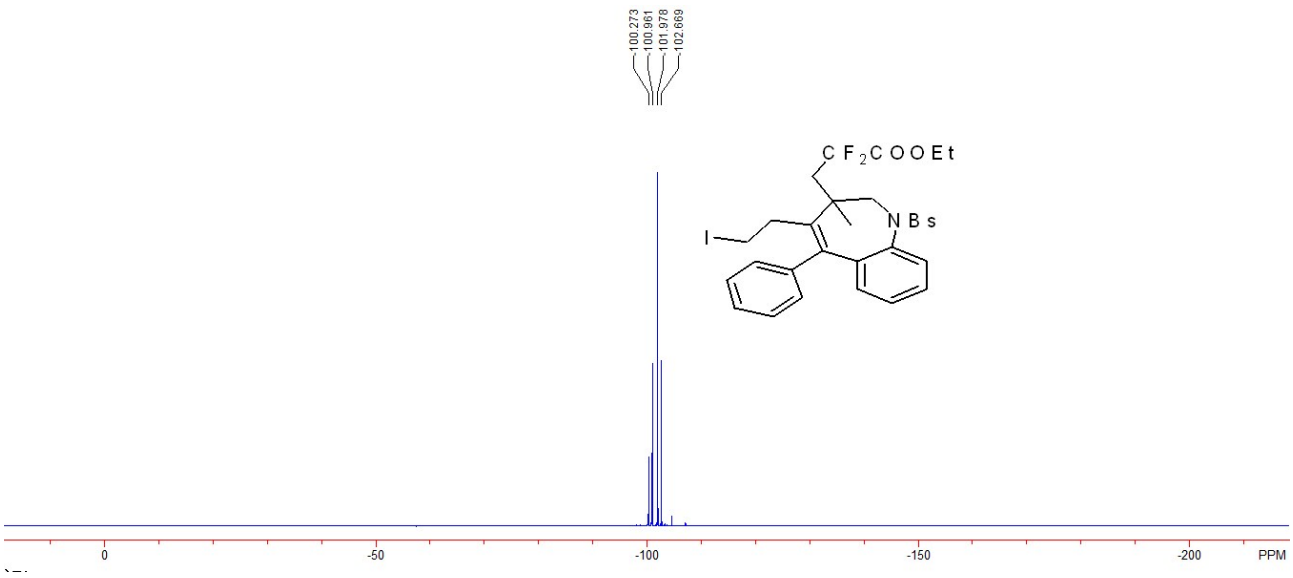



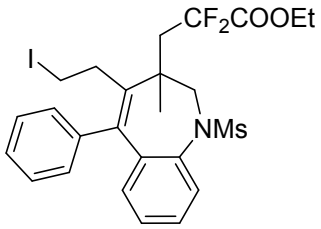




**Compound 2b**: 81 mg, 73%, A white solid, m.p. 141-143 $^{o}$C; IR ($CH_2Cl_2$): ν 3057, 2976, 2936, 2863, 1763, 1575, 1486, 1472, 1389, 1347, 1301, 1170, 1158, 1140, 1090, 1069, 1054, 1010, 880, 859, 748, 705 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.38 (s, 3H), 1.60-1.75 (m, 1H), 2.12-2.25 (m, 1H), 2.61-2.67 (m, 1H), 2.95-3.16 (m, 3H), 3.70 (d, 1H, $J$ = 13.6 Hz), 4.18 (qd, 2H, $J_1$ = 6.8 Hz, $J_2$ = 1.6 Hz), 4.56 (d, 1H, $J$ = 13.6 Hz), 6.81 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz), 6.90 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz), 7.11-7.21 (m, 4H), 7.31 (t, 1H, $J$ = 7.6 Hz), 7.36-7.39 (m, 2H), 7.68 (brs, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 13.8, 25.4, 37.6, 41.2, 43.5

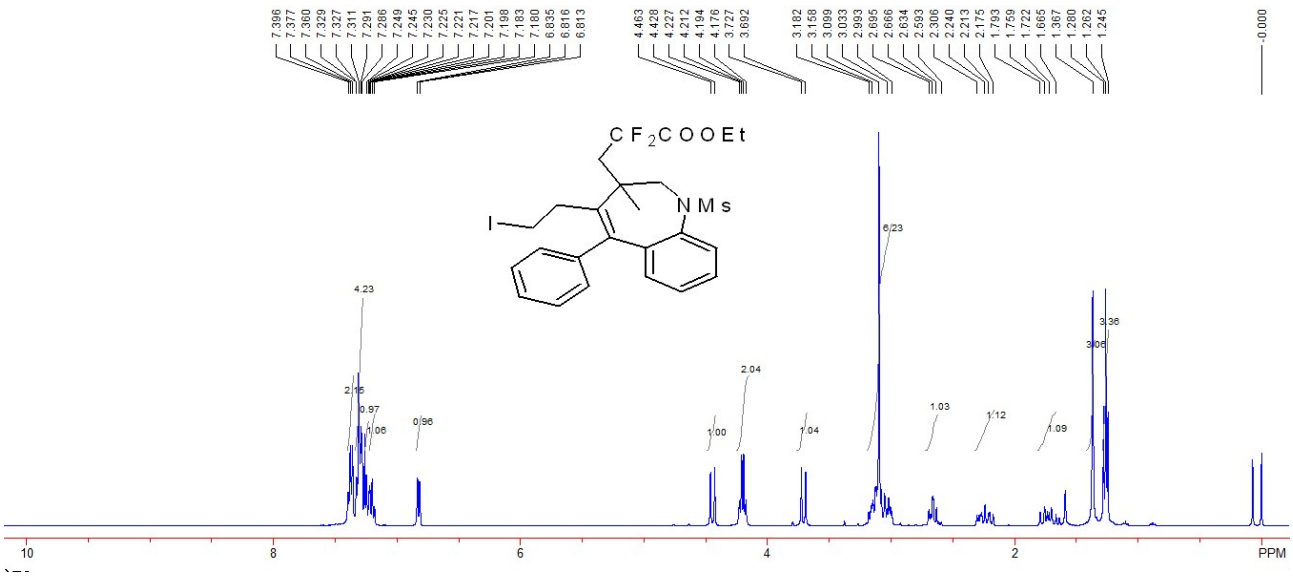
(t, $J_{C\text{-}F}$ = 21.1 Hz), 62.9, 70.2, 115.6 (t, $J_{C\text{-}F}$ = 253.1 Hz), 127.3, 127.4, 127.6, 128.2, 128.5, 128.6, 129.0, 129.1, 130.4, 132.5, 136.0, 140.1, 140.9, 142.2, 142.3, 143.5, 164.0 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.6 (d, 1F, $J$ = 258.7 Hz), -102.3 (d, 1F, $J$ = 258.7 Hz); MS (ESI) *m/z*: 744.0 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{30}H_{30}F_2INO_4S^+$ requires: 744.0086, Found: 744.0093.

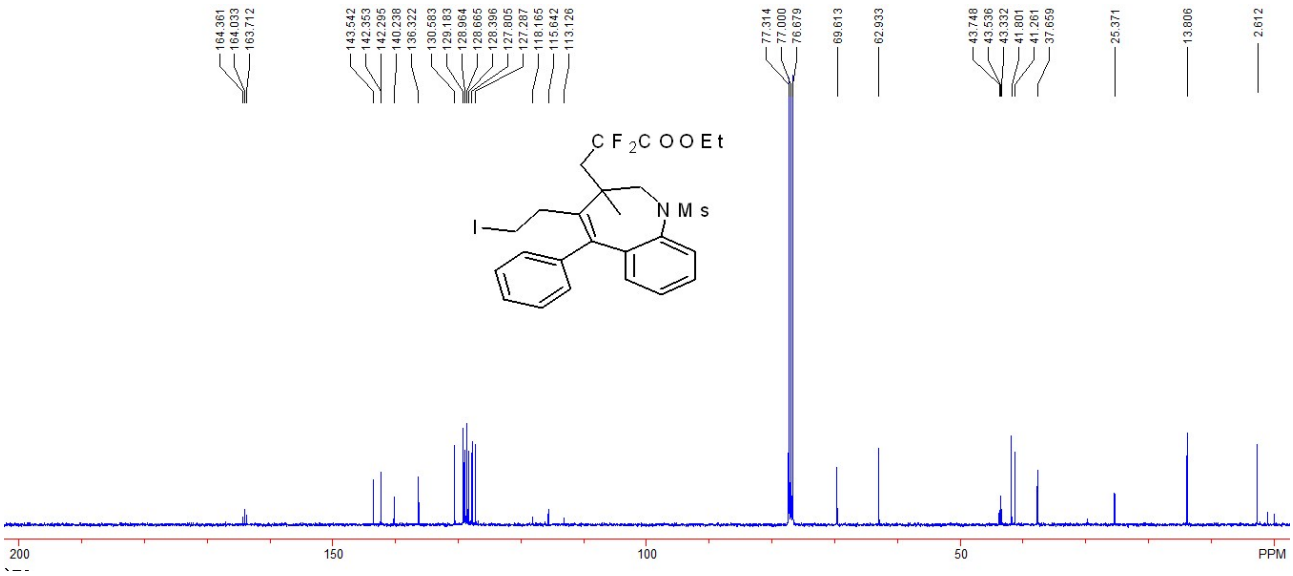


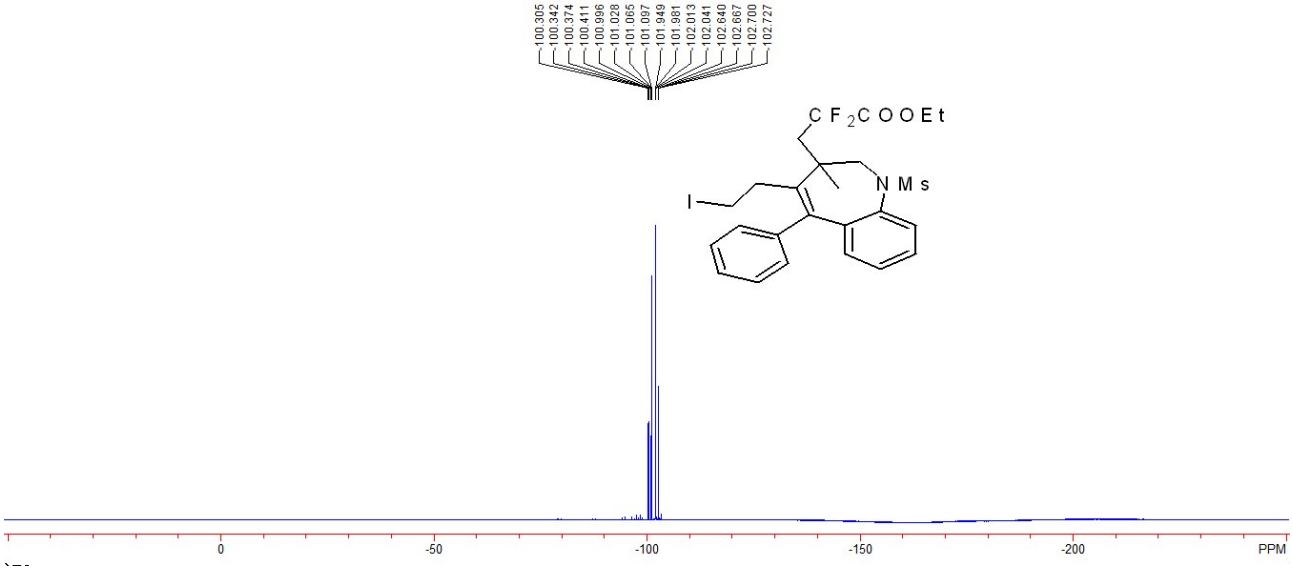


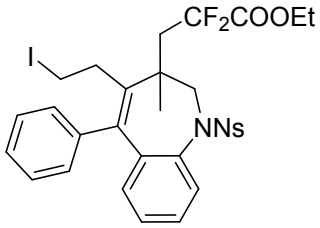




**Compound 2c**: 74 mg, 82%, A white solid, m.p. 122-124 $^{o}$C; IR ($CH_2Cl_2$): ν 2973, 2929, 2893, 1763, 1488, 1444, 1355, 1169, 1145, 1078, 1047, 964, 879, 771, 736, 705 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.26 (t, 3H, $J$ = 7.2 Hz), 1.37 (s, 3H), 1.64-1.79 (m, 1H), 2.18-2.31 (m, 1H), 2.59-2.70 (m, 1H), 2.99-3.18 (m, 6H), 3.71 (d, 1H, $J$ = 14.0 Hz), 4.18-4.23 (m, 2H), 4.45 (d, 1H, $J$ = 14.0 Hz), 6.83 (dd, 1H, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz), 7.18-7.22 (m, 1H), 7.23-7.26 (m, 2H), 7.29-7.33 (m, 4H), 7.36-7.40 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.6, 13.8, 25.4, 37.7, 41.3, 41.8, 43.5 (t, $J_{C\text{-}F}$ = 21.2 Hz), 62.9, 69.6, 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 127.3, 127.8, 128.4, 128.7, 129.0, 129.2, 130.6, 136.3, 140.2, 142.3, 142.4, 143.5, 164.0 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.7 (ddd, 1F, $J_1$ = 259.8 Hz, $J_2$ = 25.9 Hz, $J_3$ = 13.9 Hz), -102.4 (ddd, 1F, $J_1$ = 259.8 Hz, $J_2$ = 34.2 Hz, $J_3$ = 12.0 Hz); MS (ESI) *m/z*: 621.1 (M+$NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{32}F_2IN_2O_4S^+$ requires: 621.1090, Found: 621.1091.

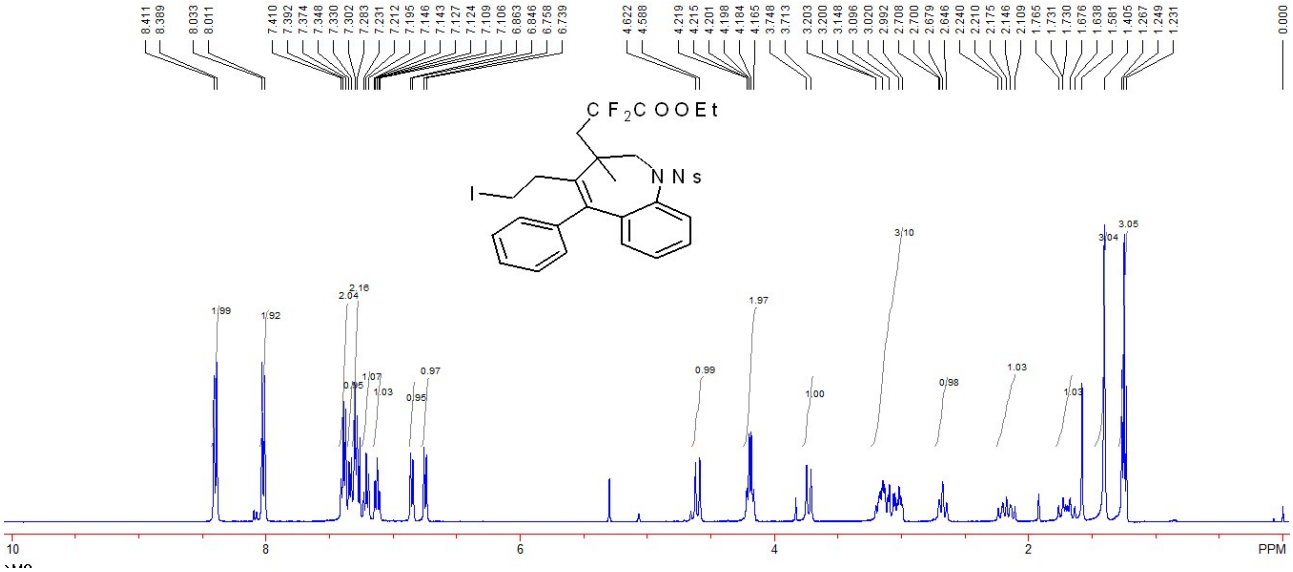

7.396
7.377
7.360
7.329
7.327
7.311
7.291
7.286
7.249
7.245
7.230
7.225
7.221
7.217
7.201
7.198
7.183
7.180
6.835
6.816
6.813
4.463
4.428
4.227
4.212
4.194
4.176
3.727
3.692
3.182
3.158
3.099
3.033
2.993
2.695
2.666
2.634
2.593
2.306
2.240
2.213
2.175
1.793
1.759
1.722
1.665
1.367
1.280
1.262
1.245
0.000
CF2COOEt
NMs
I
4.23
2.15
0.97
1.06
0.96
1.00
2.04
1.04
6.23
1.03
1.12
1.09
3.36
3.06
10
8
6
4
2
PPM

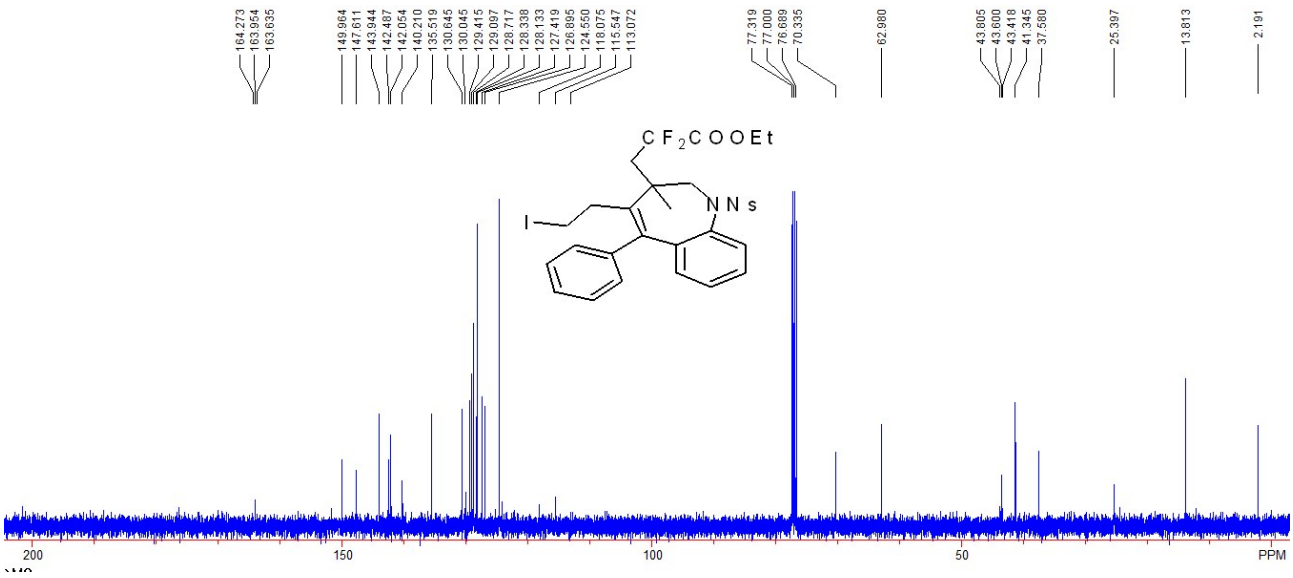

164.361
164.033
163.712
143.542
142.353
142.295
140.238
136.322
130.583
129.183
128.964
128.665
128.396
127.805
127.287
118.165
115.642
113.126
77.314
77.000
76.679
69.613
62.933
43.748
43.536
43.332
41.801
41.261
37.659
25.371
13.806
2.612
CF2COOEt
NMs
I
200
150
100
50
PPM

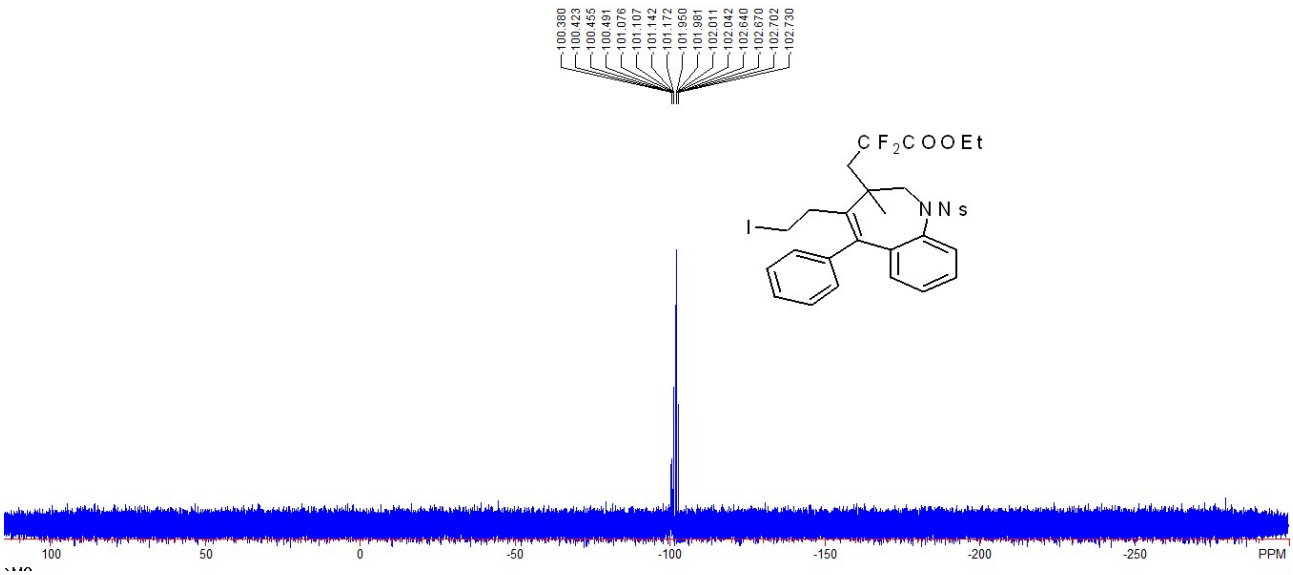

100.305
100.342
100.374
100.411
100.996
101.028
101.065
101.097
101.949
101.981
102.013
102.041
102.640
102.667
102.700
102.727
CF2COOEt
NMs
I
0
-50
-100
-150
-200
PPM

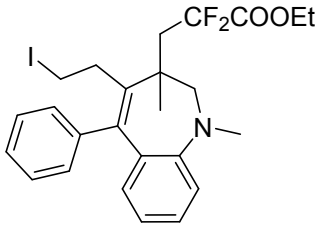



**Compound 2d**: 68 mg, 64%, A white solid, m.p. 129-131 °C; IR ($CH_2Cl_2$): ν 3019, 2970, 1765, 1531, 1485, 1346, 1307, 1171, 1159, 1085, 1048, 868, 774, 705 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.25 (t, 3H, $J$ = 7.2 Hz), 1.41 (s, 3H), 1.58-1.77 (m, 1H), 2.11-2.24 (m, 1H), 2.45-2.71 (m, 1H), 2.99-3.20 (m, 3H), 3.73 (d, 1H, $J$ = 13.6 Hz), 4.19 (qd, 2H, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz), 4.60 (d, 1H, $J$ = 14.0 Hz), 6.75 (d, 1H, $J$ = 8.4 Hz), 6.85 (d, 1H, $J$ = 6.8 Hz), 7.13 (td, 1H, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz), 7.21 (t, 1H, $J$ = 7.2 Hz), 7.29 (d, 2H, $J$ = 8.4 Hz), 7.34 (d, 1H, $J$ = 7.2 Hz), 7.39 (t, 2H, $J$ = 7.2 Hz), 8.02 (d, 2H, $J$ = 8.4 Hz), 8.40 (d, 2H, $J$ = 8.8 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 13.8, 25.4, 37.6, 41.3, 43.6 (t, $J_{C\text{-}F}$ = 20.5 Hz), 63.0, 70.3, 115.5 (t, $J_{C\text{-}F}$ = 252.8 Hz), 124.5, 126.9, 127.4, 128.1, 128.3, 128.7, 129.1, 129.4, 130.0, 130.6, 135.5, 140.2, 142.1, 142.5, 143.9, 147.6, 150.0, 164.0 (t, $J_{C\text{-}F}$ = 31.9 Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.6 (ddd, 1F, $J_1$ = 259.4 Hz, $J_2$ = 25.9 Hz, $J_3$ = 13.9 Hz), -102.3 (ddd, 1F, $J_1$ = 259.4 Hz, $J_2$ = 22.6 Hz, $J_3$ = 10.5 Hz); MS (ESI) *m/z*: 711.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{30}H_{30}F_2IN_2O_6S^+$ requires: 711.0832, Found: 711.0847.



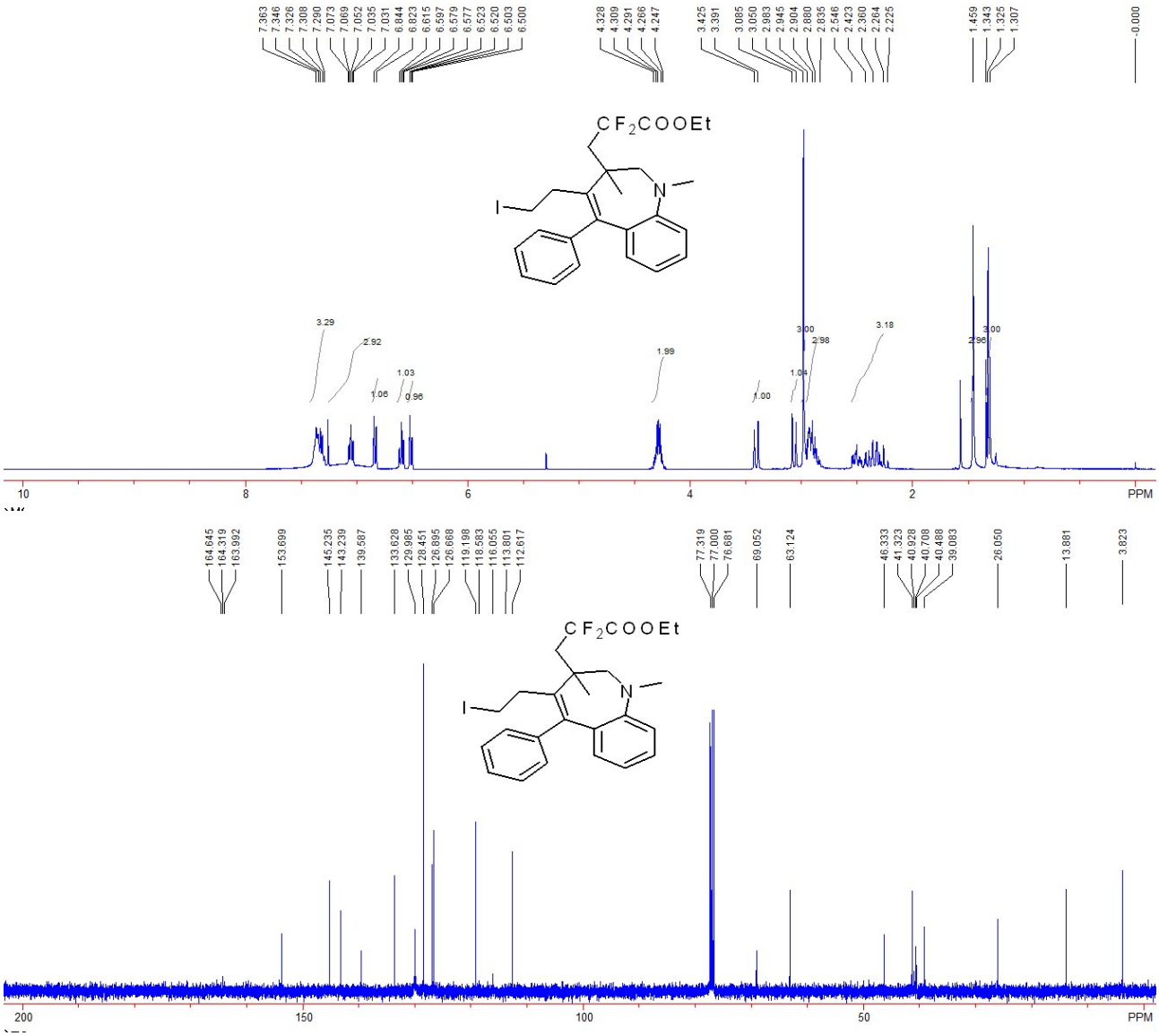


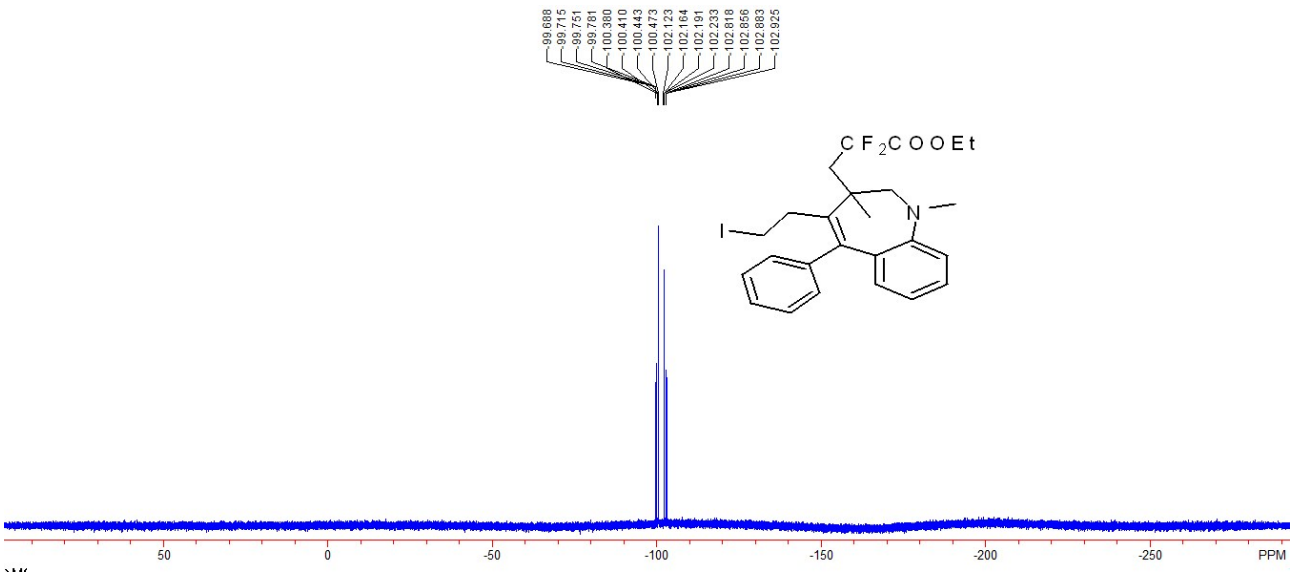



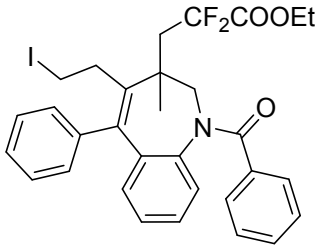




**Compound 2e**: 45 mg, 56%, A colorless oil; IR ($CH_2Cl_2$): ν 2979, 2929, 2870, 1760, 1646, 1592, 1491, 1442, 1300, 1189, 1170, 1073, 1050, 753, 707 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (t, 3H, $J$ = 7.2 Hz), 1.46 (s, 3H), 2.23-2.55 (m, 3H), 2.84-2.95 (m, 3H), 2.98 (s, 3H), 3.07 (d, 1H, $J$ = 13.6 Hz), 3.41 (d, 1H, $J$ = 13.6 Hz), 4.25-4.33 (m, 2H), 6.50 (dd, 1H, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz), 6.52-6.62 (m, 1H), 6.83 (d, 1H, $J$ = 8.4 Hz), 7.03-7.07 (m, 3H), 7.29-7.36 (m, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 3.8, 13.9, 26.1, 39.1, 40.7 (t, $J_{C-F}$ = 20.2 Hz), 41.3, 46.3, 63.1, 69.1, 112.6, 116.1 (t, $J_{C-F}$ = 252.8 Hz), 119.2, 126.7, 126.9, 128.5, 130.0, 133.6, 139.6, 143.2, 145.2,

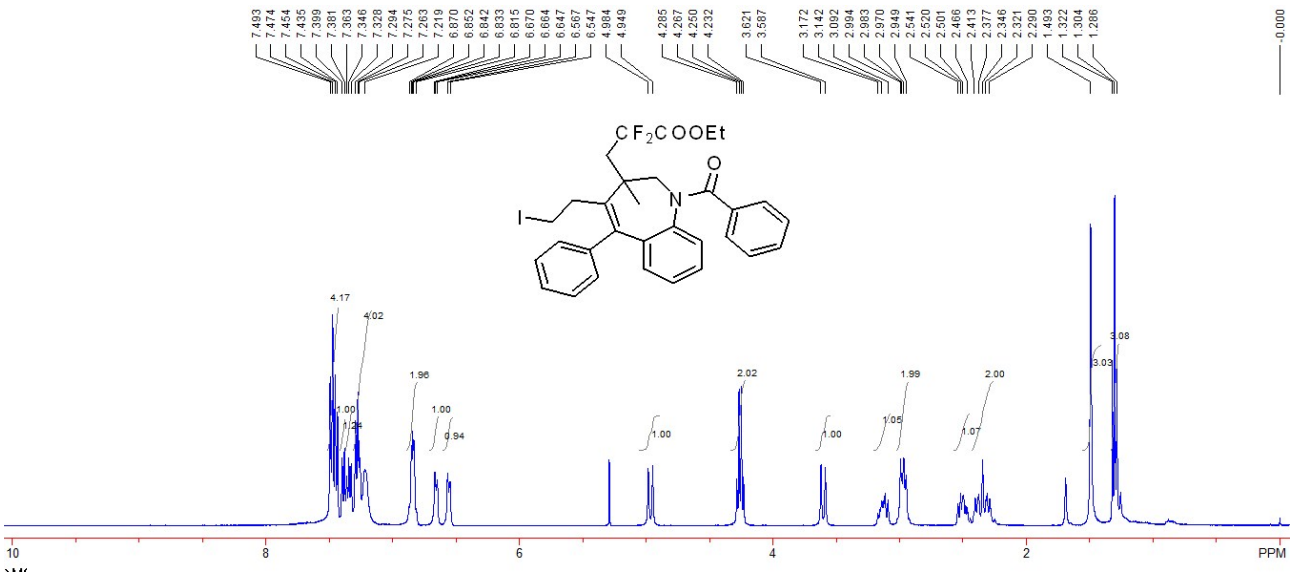
153.7, 164.3 (t, $J_{C\text{-}F}$ = 32.7 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.1 (ddd, 1F, $J_1$ = 260.2 Hz, $J_2$ = 23.7 Hz, $J_3$ = 10.2 Hz), -102.5 (ddd, 1F, $J_1$ = 260.2 Hz, $J_2$ = 25.9 Hz, $J_3$ = 15.8 Hz); MS (ESI) *m/z*: 540.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{25}H_{29}F_2INO_2^+$ requires: 540.1206, Found: 540.1208.

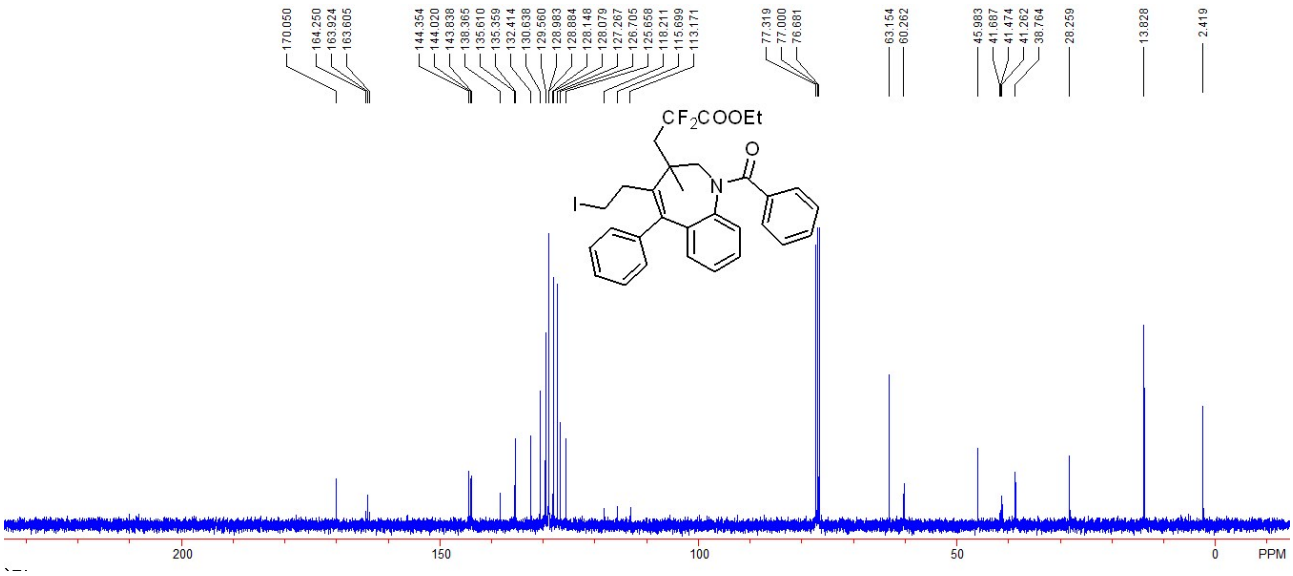


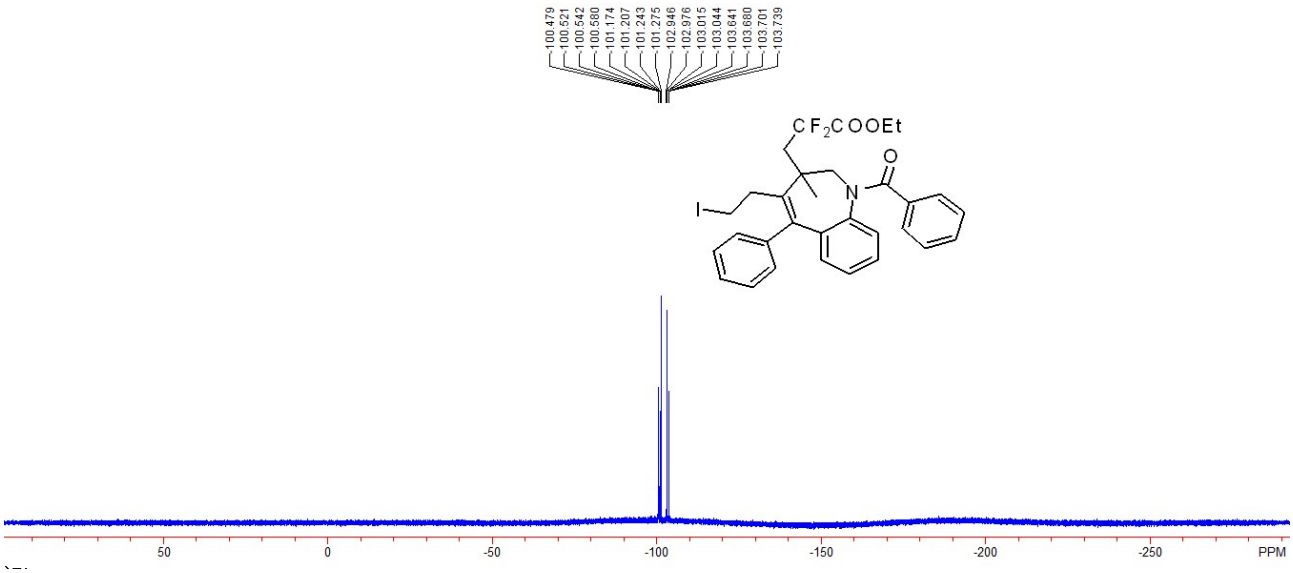


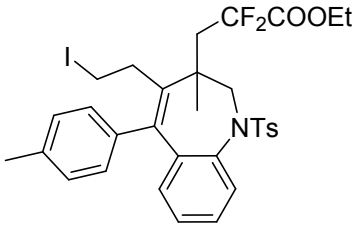




**Compound 2f**: 82 mg, 87%, A white solid, m.p. 178-180 $^{o}$C; IR ($CH_2Cl_2$): ν 3062, 2976, 2926, 1763, 1652, 1578, 1489, 1446, 1324, 1276, 1212, 1174, 1060, 762, 709 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.30 (t, 3H, $J$ = 7.2 Hz), 1.49 (s, 3H), 2.24-2.41 (m, 2H), 2.47-2.54 (m, 1H), 2.95-2.99 (m, 2H), 3.09-3.16 (m, 1H), 3.60 (d, 1H, $J$ = 13.6 Hz), 4.26 (q, 2H, $J$ = 7.2 Hz), 4.97 (d, 1H, $J$ = 13.6 Hz), 6.56 (d, 1H, $J$ = 8.0 Hz), 6.65-6.67 (m, 1H), 6.82-6.87 (m, 2H), 7.22-7.29 (m, 4H), 7.33-7.40 (m, 2H), 7.44-7.49 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.4, 13.8, 28.3, 38.8, 41.5 (t, $J_{C\text{-}F}$ = 21.2 Hz), 46.0, 60.3, 63.2, 115.7 (t, $J_{C\text{-}F}$ = 252.8 Hz), 125.7, 126.7, 127.3, 128.1, 128.9, 129.0, 129.6, 130.6, 132.4, 135.4, 135.6, 138.4, 143.8, 144.0, 144.4, 163.9 (t, $J_{C\text{-}F}$ = 32.8 Hz), 170.1; $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.9 (ddd, 1F, $J_1$ = 257.9 Hz, $J_2$ = 23.7 Hz, $J_3$ = 15.6 Hz), -103.3 (ddd, 1F, $J_1$ = 257.9 Hz, $J_2$ = 22.6 Hz, $J_3$ = 14.7 Hz); MS (ESI) *m/z*: 630.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{31}F_2INO_3^+$ requires: 630.1311, Found: 630.1311.

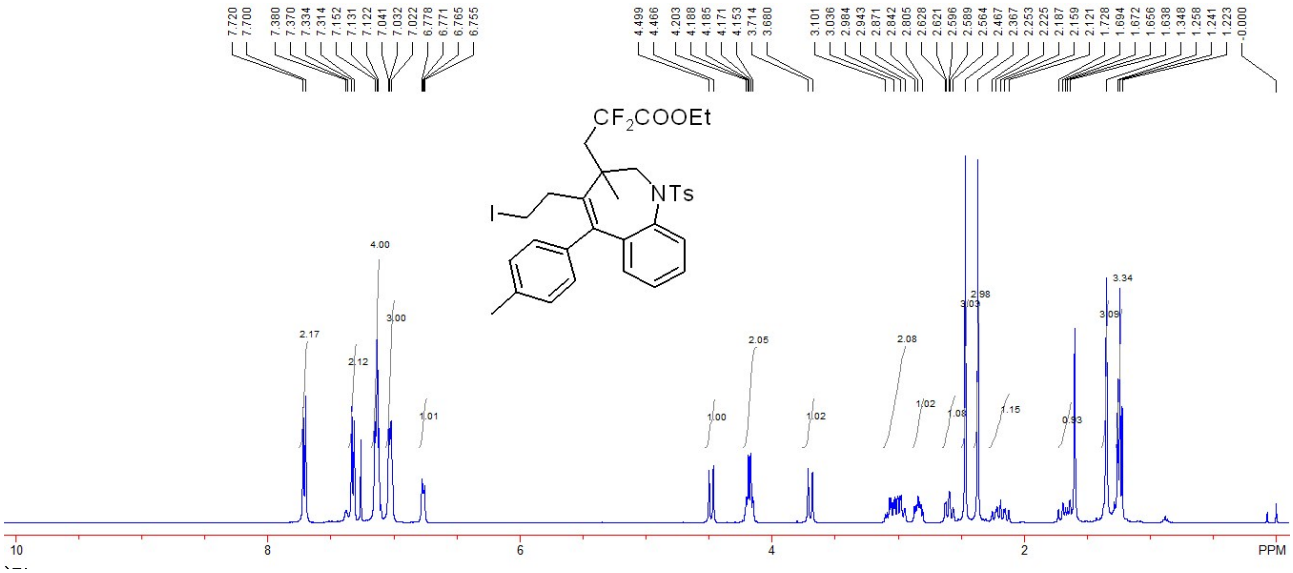

7.493
7.474
7.454
7.435
7.399
7.381
7.363
7.346
7.328
7.294
7.275
7.263
7.219
6.870
6.852
6.842
6.833
6.815
6.670
6.664
6.647
6.567
6.547
4.984
4.949
4.285
4.267
4.250
4.232
3.621
3.587
3.172
3.142
3.092
2.994
2.983
2.970
2.949
2.541
2.520
2.501
2.466
2.413
2.377
2.346
2.321
2.290
1.493
1.322
1.304
1.286
0.000
CF2COOEt
O
N
I
4.17
4.02
1.96
1.00
1.24
1.00
0.94
1.00
2.02
1.00
1.99
1.05
2.00
1.07
3.08
3.03
10
8
6
4
2
PPM

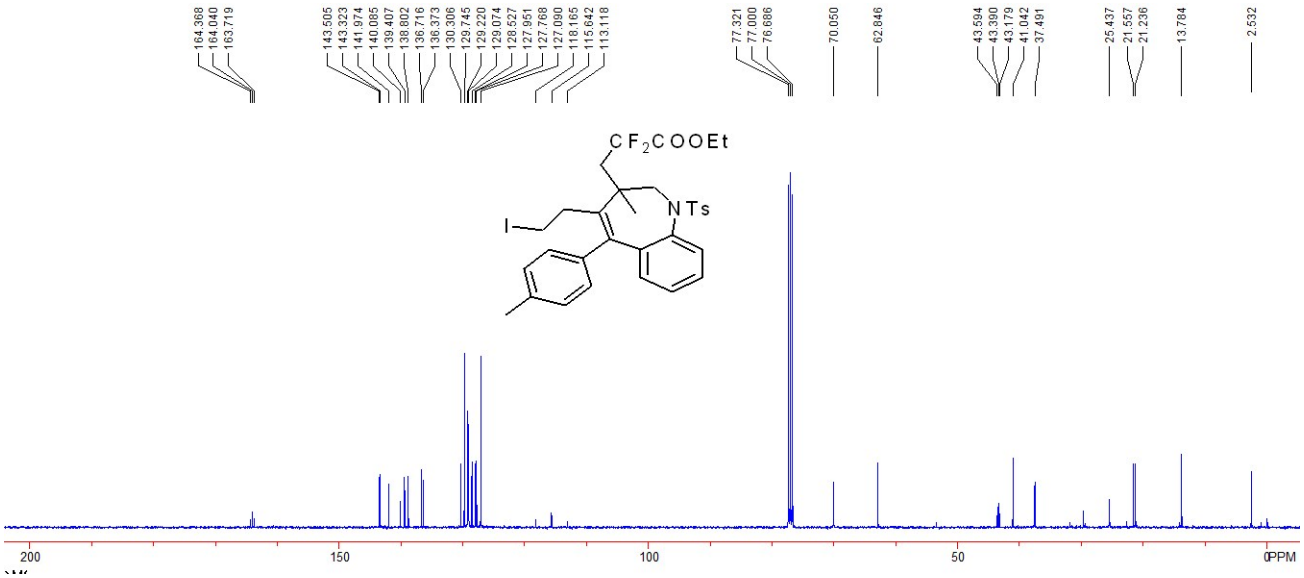

170.050
164.250
163.924
163.605
144.354
144.020
143.838
138.365
135.610
135.359
132.414
130.638
129.560
128.983
128.884
128.148
128.079
127.267
126.705
125.658
118.211
115.699
113.171
77.319
77.000
76.681
63.154
60.262
45.983
41.687
41.474
41.262
38.764
28.259
13.828
2.419
CF2COOEt
O
N
I
200
150
100
50
0
PPM

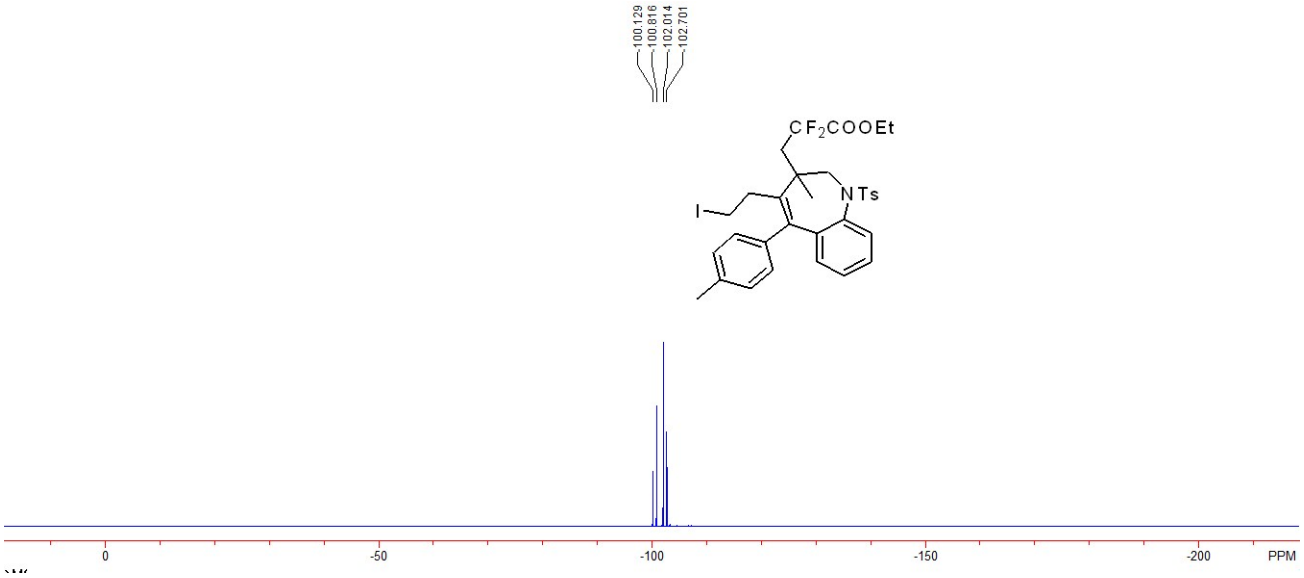

100.479
100.521
100.542
100.580
101.174
101.207
101.243
101.275
102.946
102.976
103.015
103.044
103.641
103.680
103.701
103.739
CF2COOEt
O
N
I
50
0
-50
-100
-150
-200
-250
PPM

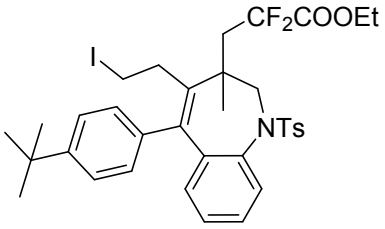



**Compound 2g**: 83 mg, 80%, A white solid, m.p. 130-132 °C; IR ($CH_2Cl_2$): ν 2979, 2926, 2859, 1764, 1597, 1487, 1444, 1344, 1303, 1154, 1139, 1091, 1037, 881, 813, 769, 734, 706 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.64 (s, 3H), 1.66-1.73 (m, 1H), 2.12-2.25 (m, 1H), 2.37 (s, 3H), 2.47 (s, 3H), 2.56-2.63 (m, 1H), 2.81-2.87 (m, 1H), 2.94-3.10 (m, 2H), 3.70 (d, 1H, $J$ = 13.6 Hz), 4.15-4.20 (m, 2H), 4.48 (d, 1H, $J$ = 13.6 Hz), 6.76-6.78 (m, 1H), 7.01-7.04 (m, 3H), 7.12-7.15 (m, 4H), 7.32 (d, 2H, $J$ = 8.0 Hz), 7.71 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.5, 13.8, 21.2, 21.6, 25.4, 37.5, 41.0, 43.4 (t, $J_{C\text{-}F}$ = 21.1 Hz), 62.8, 70.1, 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 127.1, 127.8, 128.0, 128.5, 129.1, 129.2, 129.7, 130.3, 136.4, 136.7, 138.8, 139.4, 140.1, 142.0, 143.3, 143.5, 164.0 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.5 (d, 1F, $J$ = 258.3 Hz), -102.4 (d, 1F, $J$ = 258.3 Hz); MS (ESI) *m/z*: 711.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{32}H_{38}F_2IN_2O_4S^+$ requires: 711.1560, Found: 711.1561.



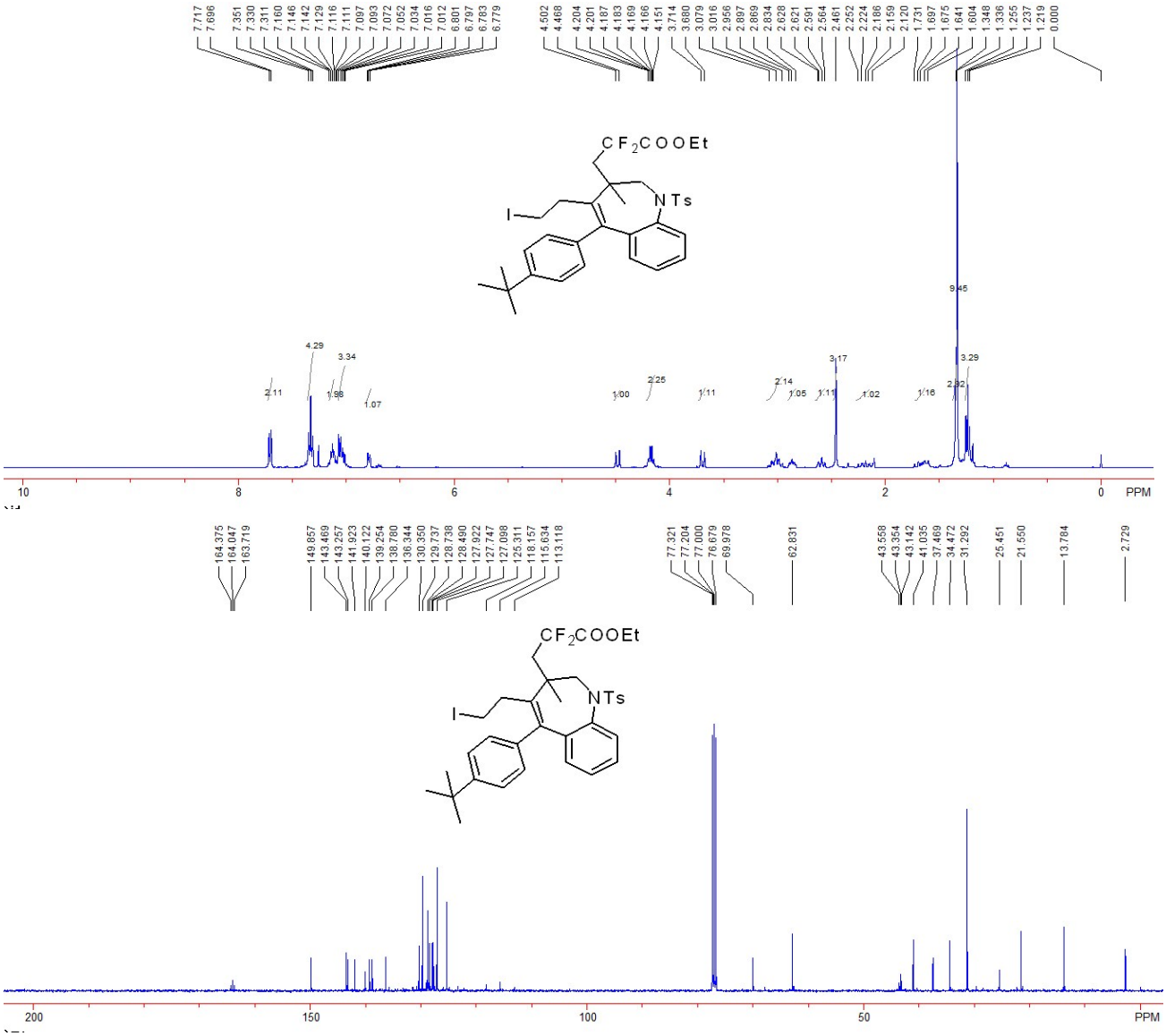


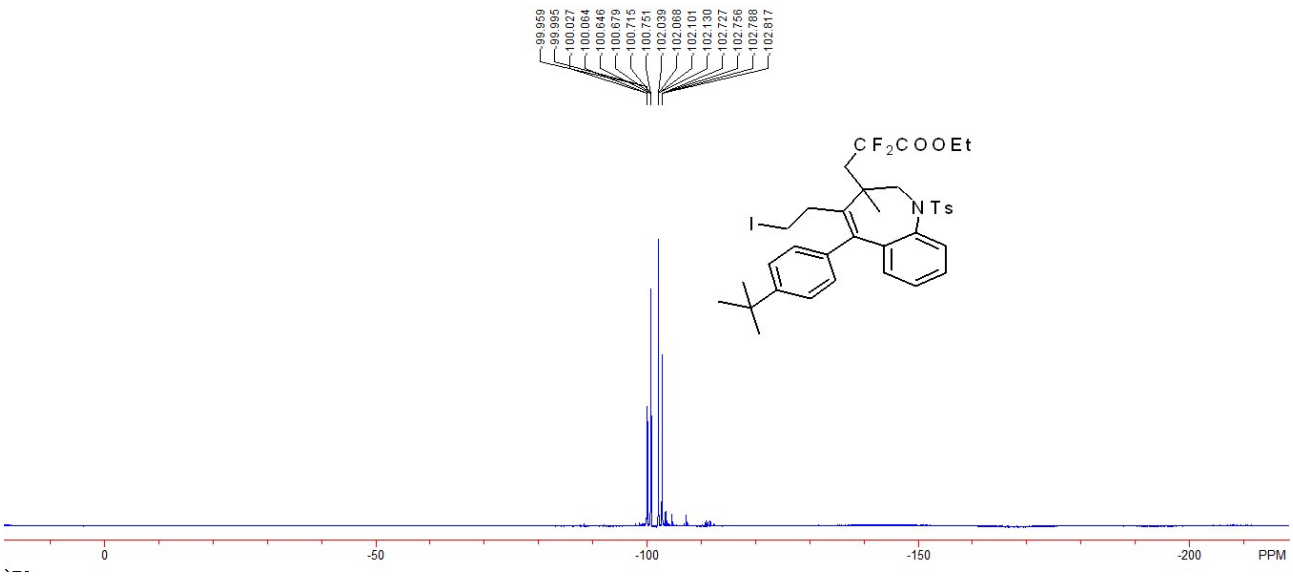



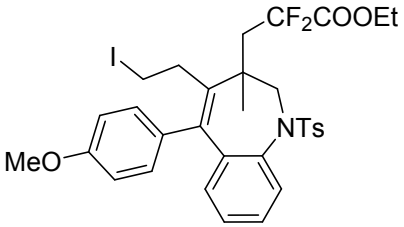




**Compound 2h**: 91 mg, 83%, A white solid, m.p. 143-145 $^{o}$C; IR ($CH_2Cl_2$): ν 2966, 2898, 2865, 1764, 1487, 1447, 1342, 1303, 1155, 1139, 1091, 1049, 880, 846, 769, 705 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.34 (s, 9H), 1.35 (s, 3H), 1.64-1.73 (m, 1H), 2.11-2.25 (m, 1H), 2.46 (s, 3H), 2.56-2.63 (m, 1H), 2.83-2.90 (m, 1H), 2.96-3.09 (m, 2H), 3.70 (d, 1H, $J$ = 13.6 Hz), 4.18 (qd, 2H, $J_1$ = 6.8 Hz, $J_2$ = 1.2 Hz), 4.49 (d, 1H, $J$ = 13.6 Hz), 6.79 (dd, 1H, $J_1$ = 7.2 Hz, $J_2$ = 1.6 Hz), 6.70-7.09 (m, 3H), 7.11-7.16 (m, 2H), 7.31-7.35 (m, 4H), 7.70 (d, 2H, $J$ = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.7, 13.8, 21.6, 25.5, 31.3, 34.5, 37.5, 41.0, 43.4 (t, $J_{C-F}$ =

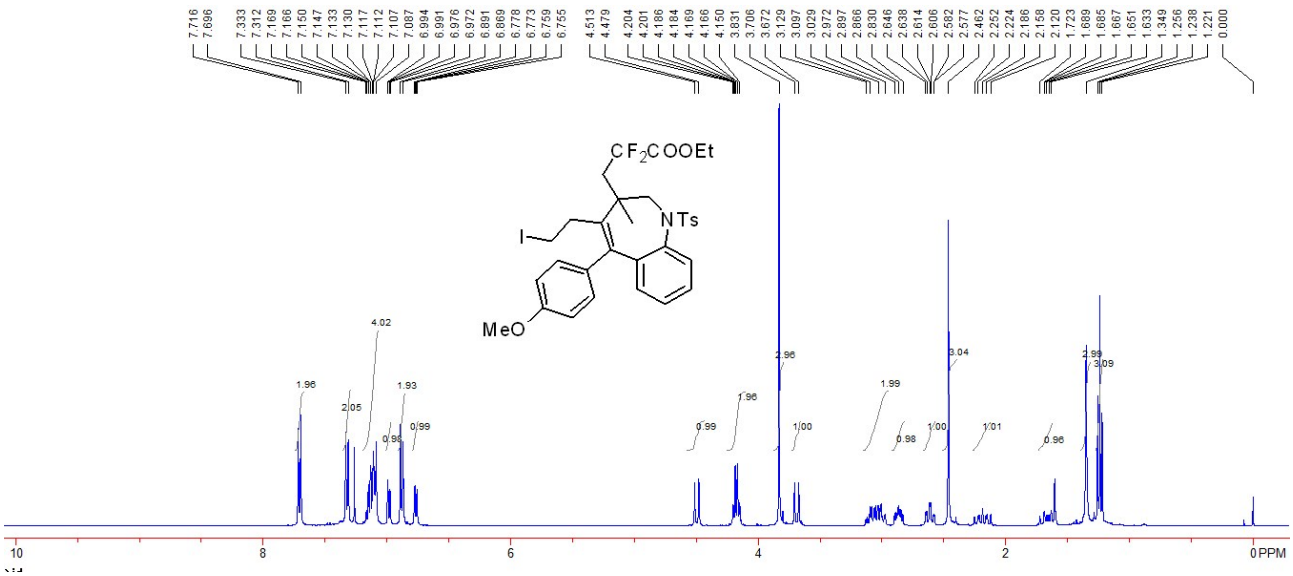
21.1 Hz), 62.8, 70.0, 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 125.3, 127.1, 127.7, 127.9, 128.5, 128.7, 129.7, 130.4, 136.3, 138.8, 139.3, 140.1, 141.9, 143.3, 143.5, 149.9, 164.0 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.4 (ddd, 1F, $J_1$ = 258.3 Hz, $J_2$ = 25.6 Hz, $J_3$ = 13.5 Hz), -102.4 (ddd, 1F, $J_1$ = 258.3 Hz, $J_2$ = 23.3 Hz, $J_3$ = 10.9 Hz); MS (ESI) *m/z*: 753.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{35}H_{44}F_2IN_2O_4S^+$ requires: 753.2029, Found: 753.2026.

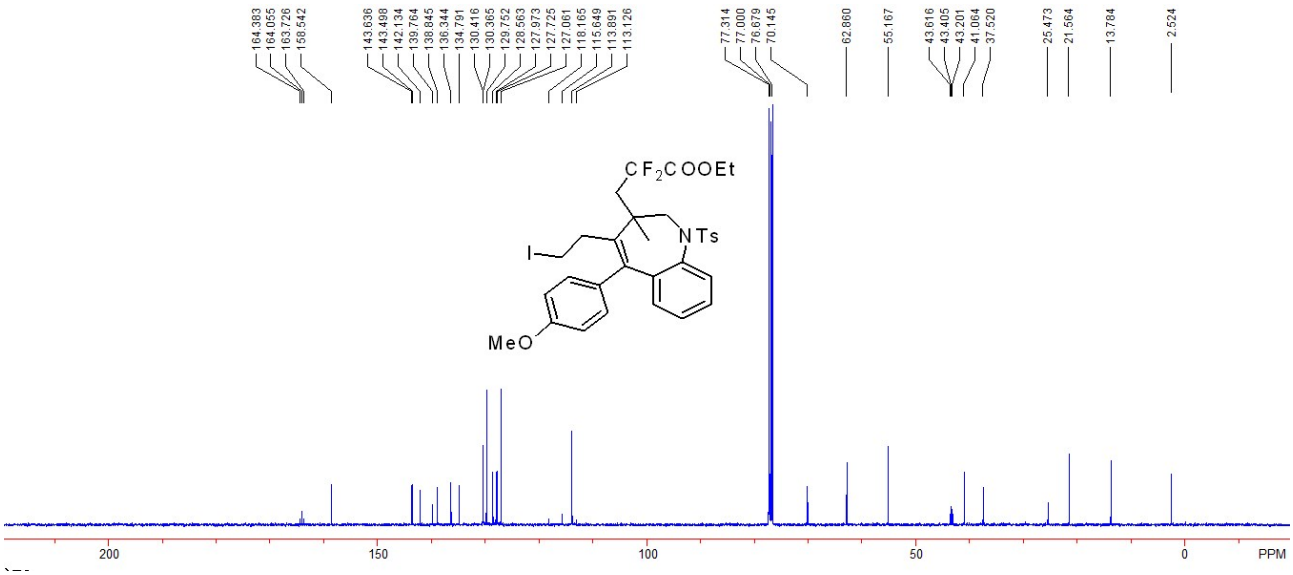


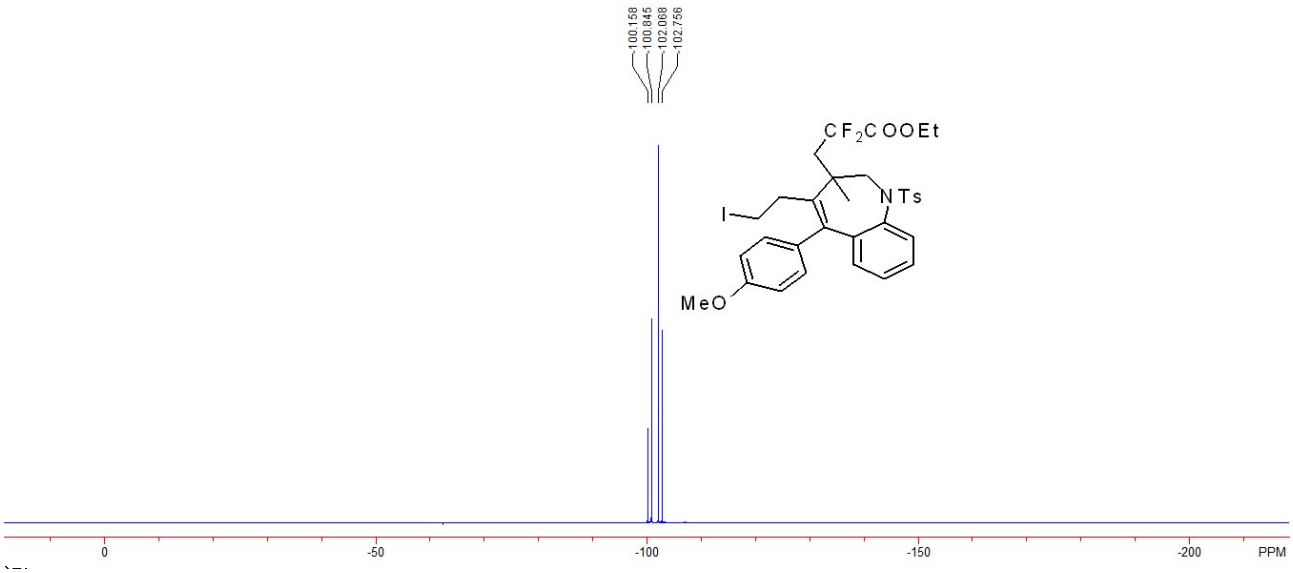


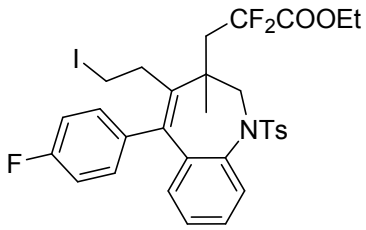




**Compound 2i**: 90 mg, 85%, A white solid, m.p. 123-125 $^{o}$C; IR ($CH_2Cl_2$): ν 3070, 2974, 2926, 2859, 1764, 1607, 1508, 1486, 1445, 1342, 1287, 1196, 1169, 1156, 1092, 1078, 1033, 880, 777, 737, 705 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.35 (s, 3H), 1.63-1.72 (m, 1H), 2.12-2.25 (m, 1H), 2.46 (s, 3H), 2.58-2.65 (m, 1H), 2.83-2.90 (m, 1H), 2.97-3.13 (m, 2H), 3.69 (d, 1H, $J$ = 13.6 Hz), 3.83 (s, 3H), 4.18 (qd, 2H, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz), 4.50 (d, 1H, $J$ = 13.6 Hz), 6.77 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz), 6.88 (d, 2H, $J$ = 8.8 Hz), 6.98 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz), 7.09-7.17 (m, 4H), 7.32 (d, 2H, $J$ = 8.0 Hz), 7.71 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.5, 13.8, 21.6, 25.5, 37.5, 41.1, 43.4 (t, $J_{C\text{-}F}$ = 21.1 Hz), 55.2, 62.9, 70.1, 113.9, 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 127.1, 127.7, 128.0, 128.6, 129.8, 130.37, 130.42, 134.8, 136.3, 138.8, 139.8, 142.1, 143.5, 143.6, 158.5, 164.1 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.5 (d, 1F, $J$ = 258.3 Hz), -102.4 (d, 1F, $J$ = 258.3 Hz); MS (ESI) *m/z*: 727.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{32}H_{38}F_2IN_2O_5S^+$ requires: 727.1509, Found: 727.1506.

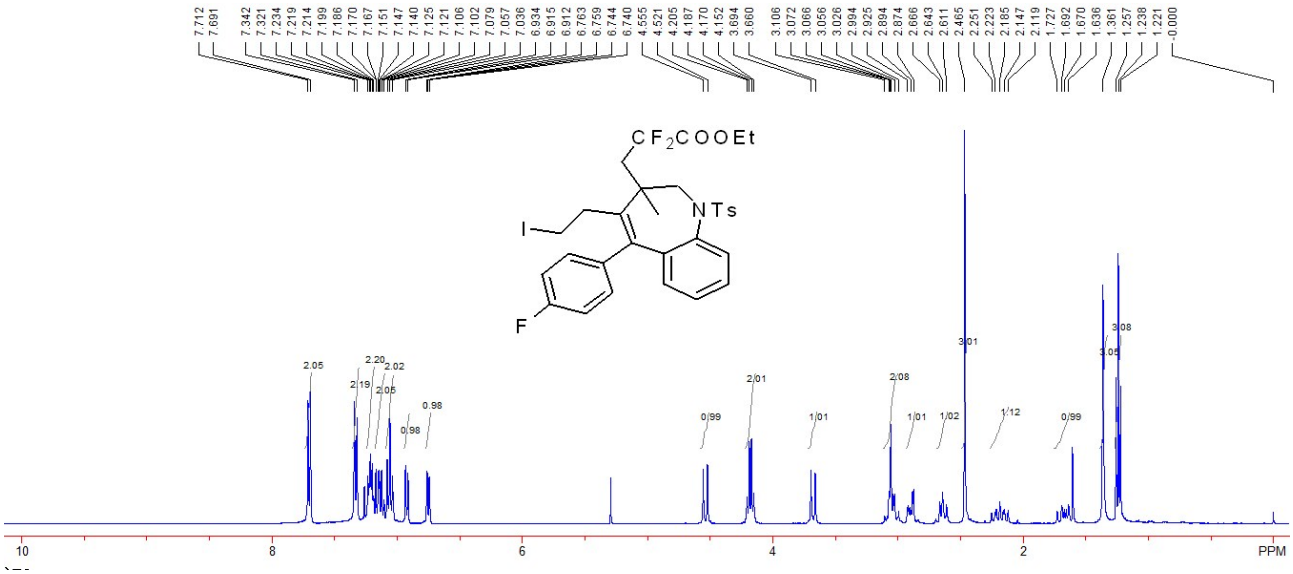

7.716
7.696
7.333
7.312
7.169
7.166
7.150
7.147
7.133
7.130
7.117
7.112
7.107
7.087
6.994
6.991
6.976
6.972
6.891
6.869
6.778
6.773
6.759
6.755
4.513
4.479
4.204
4.201
4.186
4.184
4.169
4.166
4.150
3.931
3.706
3.672
3.129
3.097
3.029
2.972
2.897
2.866
2.830
2.646
2.638
2.614
2.606
2.582
2.577
2.462
2.252
2.224
2.186
2.158
2.120
1.723
1.689
1.685
1.667
1.651
1.633
1.349
1.256
1.238
1.221
0.000
CF2COOEt
NTs
I
MeO
1.96
4.02
2.05
1.93
0.96
0.99
0.99
1.96
2.96
1.00
1.99
0.98
1.00
3.04
1.01
0.96
2.99
3.09
10
8
6
4
2
0PPM

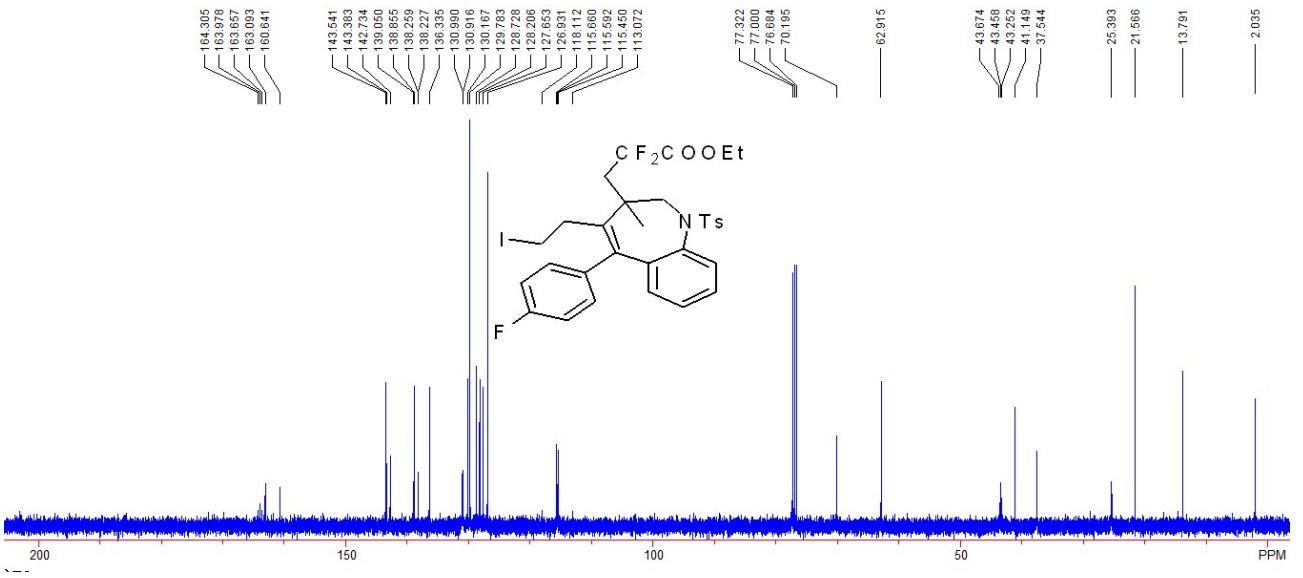

164.383
164.055
163.726
158.542
143.636
143.498
142.134
139.764
138.845
136.344
134.791
130.416
130.365
129.752
128.563
127.973
127.725
127.061
118.165
115.649
113.891
113.126
77.314
77.000
76.679
70.145
62.860
55.167
43.616
43.405
43.201
41.064
37.520
25.473
21.564
13.784
2.524
CF2COOEt
NTs
I
MeO
200
150
100
50
0
PPM

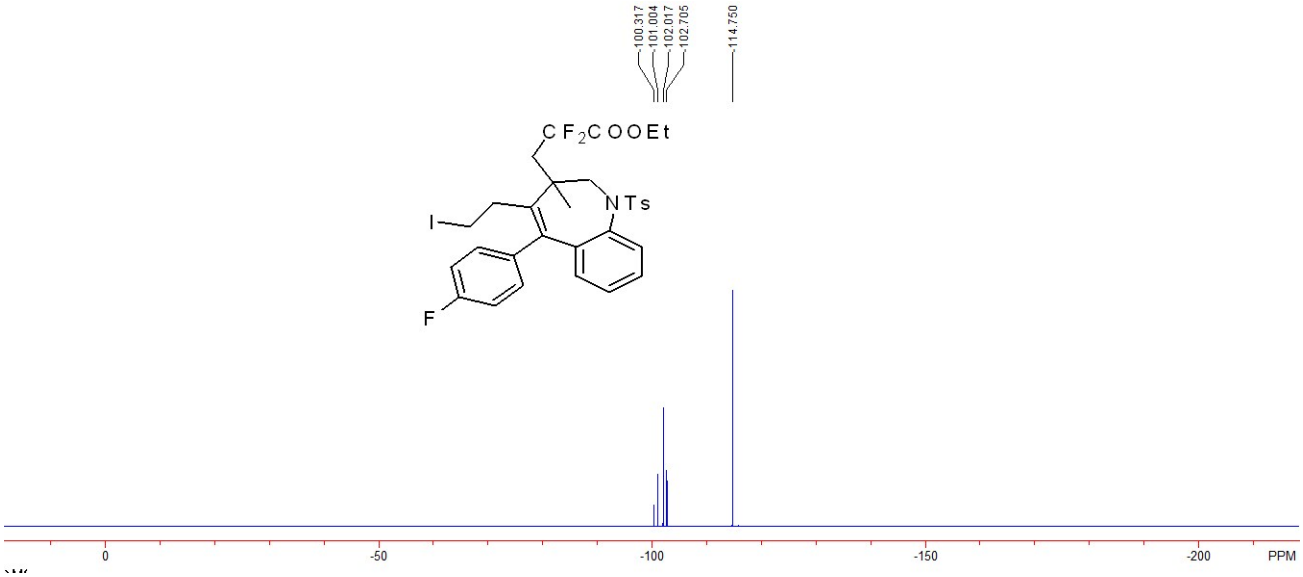

100.158
100.845
102.069
102.756
CF2COOEt
NTs
I
MeO
0
-50
-100
-150
-200
PPM

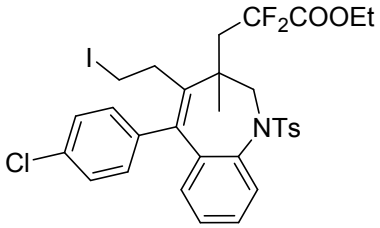



**Compound 2j**: 68 mg, 65%, A white solid, m.p. 129-131 $^{o}$C; IR ($CH_2Cl_2$): ν 2976, 2929, 2895, 1766, 1506, 1448, 1341, 1157, 1091, 1046, 879, 766, 737, 657 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.36 (s, 3H), 1.64-1.73 (m, 1H), 2.12-2.25 (m, 1H), 2.47 (s, 3H), 2.61-2.67 (m, 1H), 2.87-2.93 (m, 1H), 2.99-3.11 (m, 2H), 3.68 (d, 1H, $J$ = 13.6 Hz), 4.18 (qd, 2H, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz), 4.54 (d, 1H, $J$ = 13.6 Hz), 6.75 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz), 6.93 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz), 7.04-7.10 (m, 2H), 7.12-7.15 (m, 2H), 7.17-7.26 (m, 2H), 7.33 (d, 2H, $J$ = 8.0 Hz), 7.70 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.0, 13.8, 21.6, 25.4, 37.6, 41.2, 43.5 (t, $J_{C\text{-}F}$ = 21.2 Hz), 62.9, 70.2, 115.57 (d, $J_{C\text{-}F}$ = 21.1 Hz), 115.63 (t, $J_{C\text{-}F}$ = 252.3 Hz), 127.0, 127.7, 128.2, 128.7, 129.8, 130.2, 131.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 136.4, 138.3 (d, $J_{C\text{-}F}$ = 3.7 Hz), 138.9, 139.1, 142.8, 143.4, 143.5, 161.9 (d, $J_{C\text{-}F}$ = 245.0 Hz), 164.0 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.7 (d, 1F, $J$ = 258.3 Hz), -102.4 (d, 1F, $J$ = 258.3 Hz), -114.8 (s, 1F); MS (ESI) *m/z*: 715.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{35}F_3IN_2O_4S^+$ requires: 715.1309, Found: 715.1306.



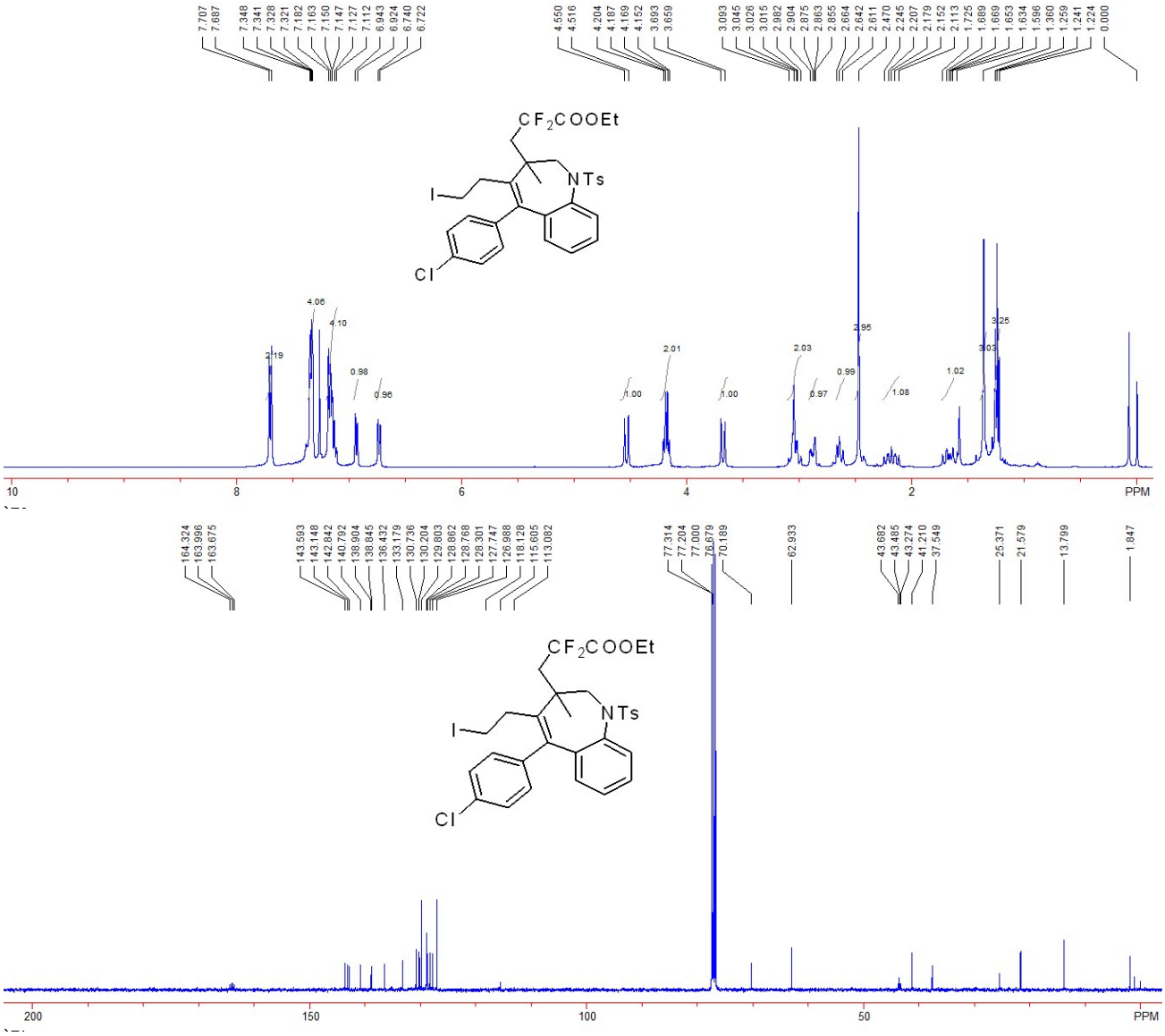


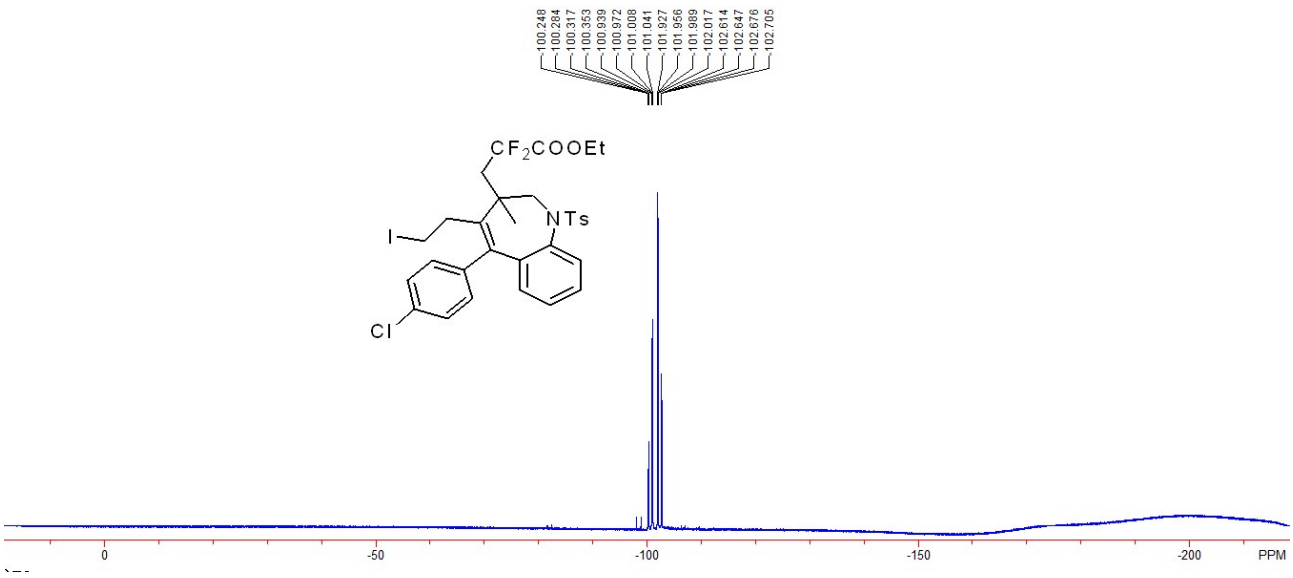



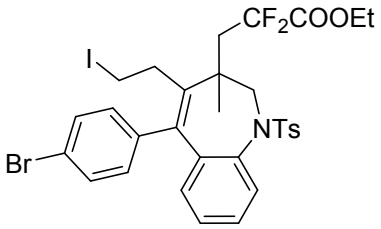




**Compound 2k**: 76 mg, 71%, A white solid, m.p. 139-141 $^{o}$C; IR ($CH_2Cl_2$): ν 3056, 2979, 2934, 2854, 1765, 1486, 1450, 1342, 1304, 1168, 1156, 1090, 1054, 1016, 861, 770, 658 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.36 (s, 3H), 1.60-1.73 (m, 1H), 2.11-2.25 (m, 1H), 2.47 (s, 3H), 2.61-2.70 (m, 1H), 2.86-2.90 (m, 1H), 2.98-3.09 (m, 2H), 3.68 (d, 1H, $J$ = 13.6 Hz), 4.15-4.20 (m, 2H), 4.53 (d, 1H, $J$ = 13.6 Hz), 6.73 (d, 1H, $J$ = 7.2 Hz), 6.93 (d, 1H, $J$ = 7.6 Hz), 7.11-7.18 (m, 4H), 7.32-7.35 (m, 4H), 7.70 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 1.8, 13.8, 21.6, 25.4, 37.5, 41.2, 43.5 (t, $J_{C\text{-}F}$ = 21.1 Hz), 62.9, 70.2, 115.6 (t, $J_{C\text{-}F}$ = 252.3

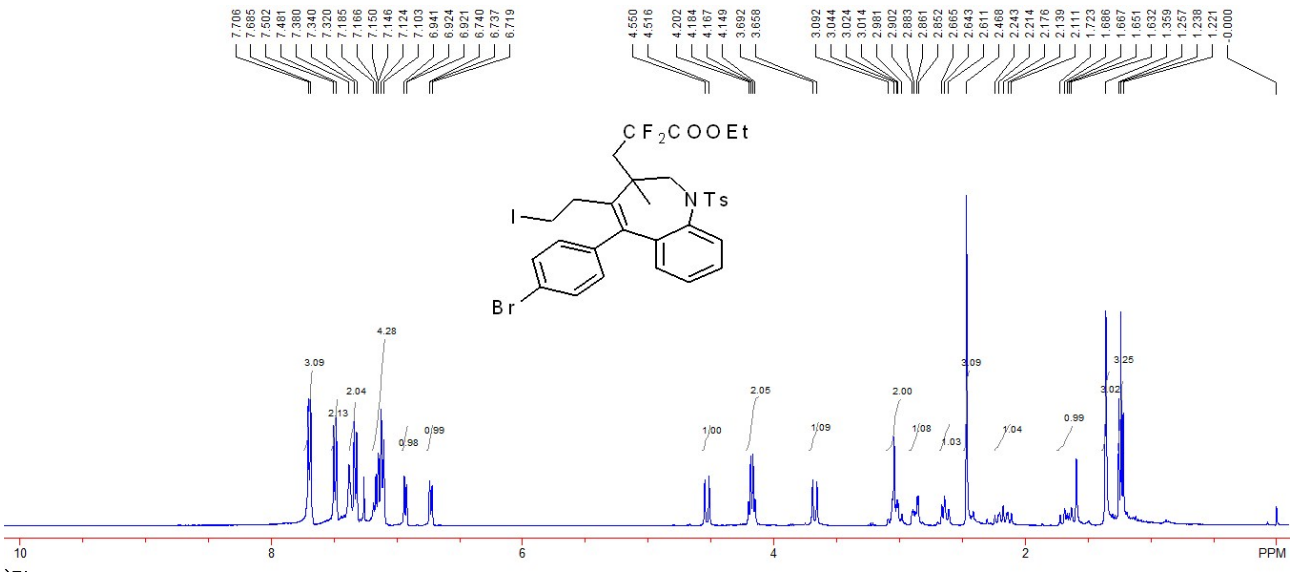
Hz), 127.0, 127.7, 128.3, 128.8, 128.9, 129.8, 130.2, 130.7, 133.2, 136.4, 138.8, 138.9, 140.8, 142.8, 143.1, 143.6, 164.0 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.7 (ddd, 1F, $J_1$ = 259.8 Hz, $J_2$ = 25.9 Hz, $J_3$ = 13.5 Hz), -102.3 (ddd, 1F, $J_1$ = 259.8 Hz, $J_2$ = 23.3 Hz, $J_3$ = 10.9 Hz); MS (ESI) *m/z*: 731.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{35}ClF_2IN_2O_4S^+$ requires: 731.1013, Found: 731.1011.

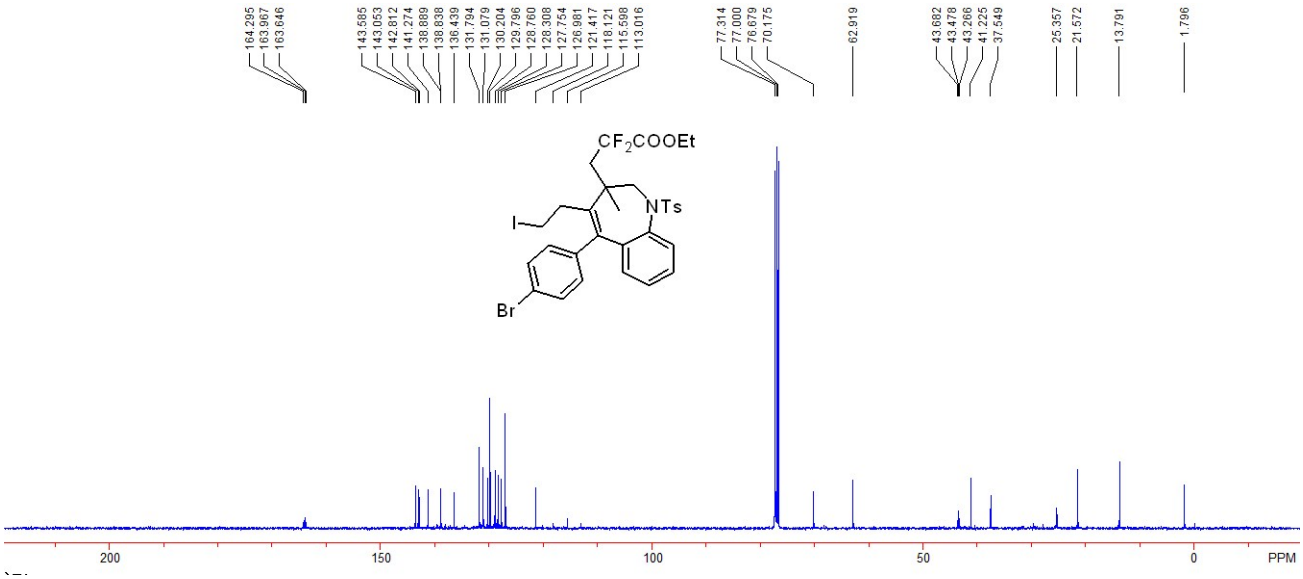


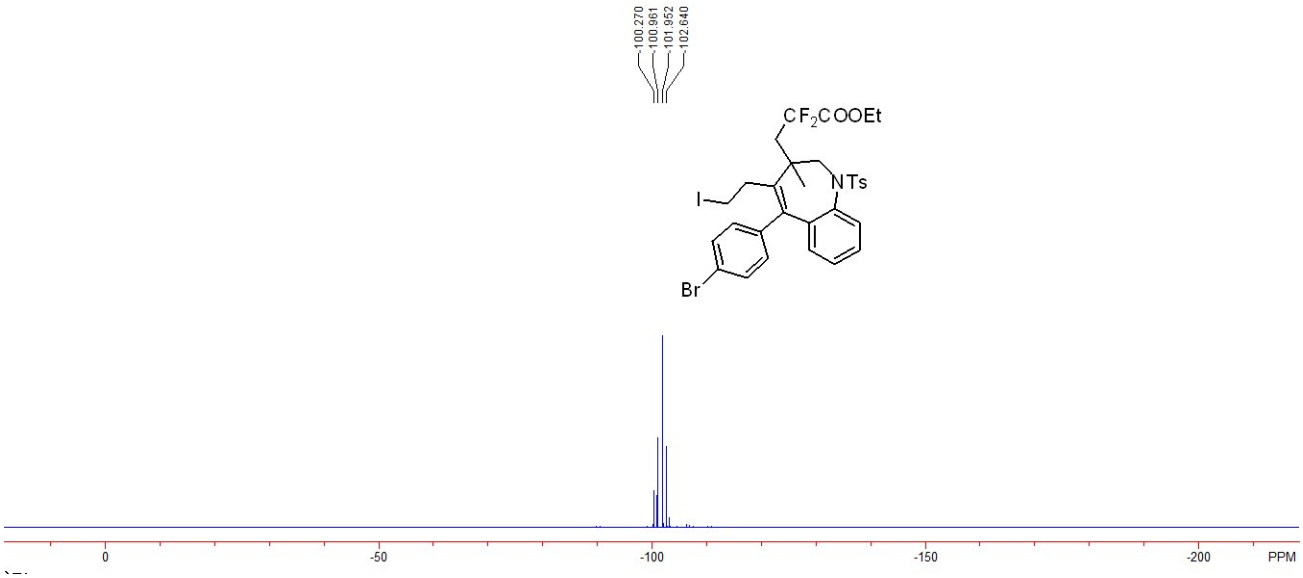


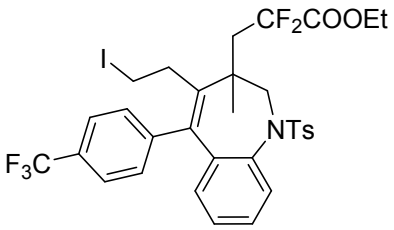




**Compound 2l**: 77 mg, 68%, A white solid, m.p. 148-150 $^{o}$C; IR ($CH_2Cl_2$): ν 2974, 2924, 2868, 1764, 1484, 1447, 1341, 1304, 1155, 1091, 1078, 1052, 1011, 860, 814, 769, 657 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.36 (s, 3H), 1.63-1.72 (m, 1H), 2.11-2.24 (m, 1H), 2.47 (s, 3H), 2.61-2.67 (m, 1H), 2.85-2.90 (m, 1H), 2.98-3.09 (m, 2H), 3.68 (d, 1H, $J$ = 13.6 Hz), 4.18 (qd, 2H, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz), 4.53 (d, 1H, $J$ = 13.6 Hz), 6.73 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz), 6.92 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz), 7.10-7.19 (m, 4H), 7.33 (d, 2H, $J$ = 7.6 Hz), 7.49 (d, 2H, $J$ = 7.6 Hz), 7.69 (d, 2H, $J$ = 7.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 1.8, 13.8, 21.6, 25.4, 37.5, 41.2, 43.5 (t, $J_{C\text{-}F}$ = 21.1 Hz), 62.9, 70.2, 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 121.4, 127.0, 127.8, 128.3, 128.8, 129.8, 130.2, 131.1, 131.8, 136.4, 138.8, 138.9, 141.3, 142.8, 143.1, 143.6, 164.0 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.6 (d, 1F, $J$ = 258.7 Hz), -102.3 (d, 1F, $J$ = 258.7 Hz); MS (ESI) *m/z*: 775.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{35}BrF_2IN_2O_4S^+$ requires: 775.0508, Found: 775.0505.

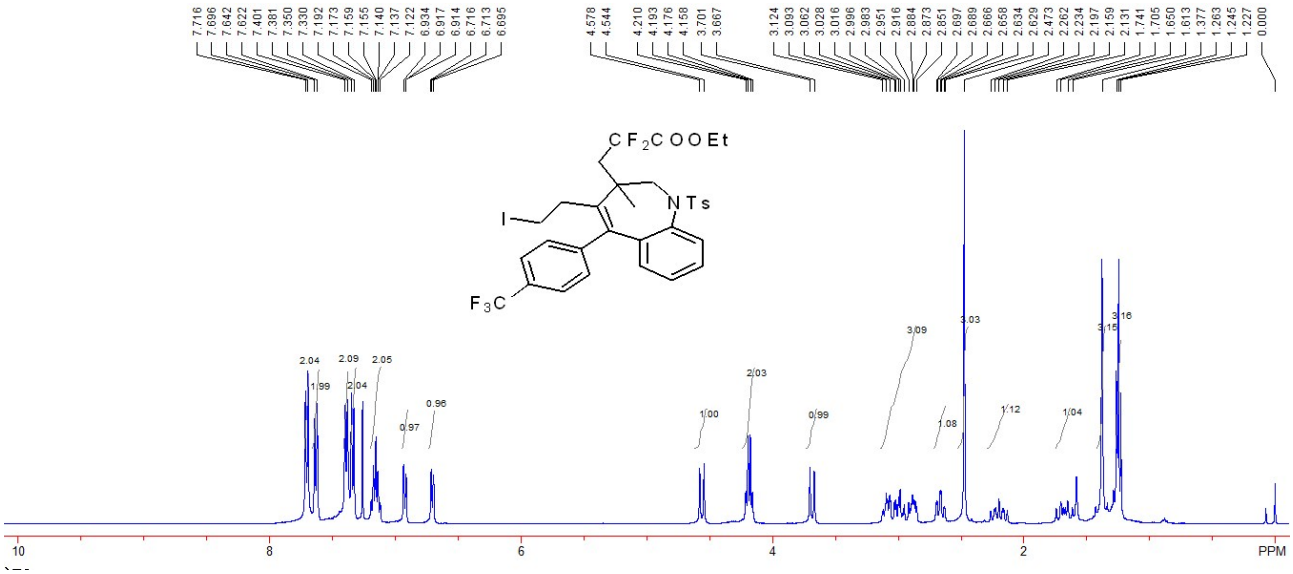

7.706
7.685
7.502
7.481
7.380
7.340
7.320
7.185
7.166
7.150
7.146
7.124
7.103
6.941
6.924
6.921
6.740
6.737
6.719
4.550
4.516
4.202
4.184
4.167
4.149
3.692
3.658
3.092
3.044
3.024
3.014
2.981
2.902
2.883
2.861
2.852
2.665
2.643
2.611
2.468
2.243
2.214
2.176
2.139
2.111
1.723
1.686
1.667
1.651
1.632
1.359
1.257
1.238
1.221
-0.000
CF2COOEt
NTs
I
Br
3.09
2.13
2.04
4.28
0.98
0.99
1.00
2.05
1.09
2.00
1.08
1.03
3.09
1.04
0.99
3.02
3.25
10
8
6
4
2
PPM

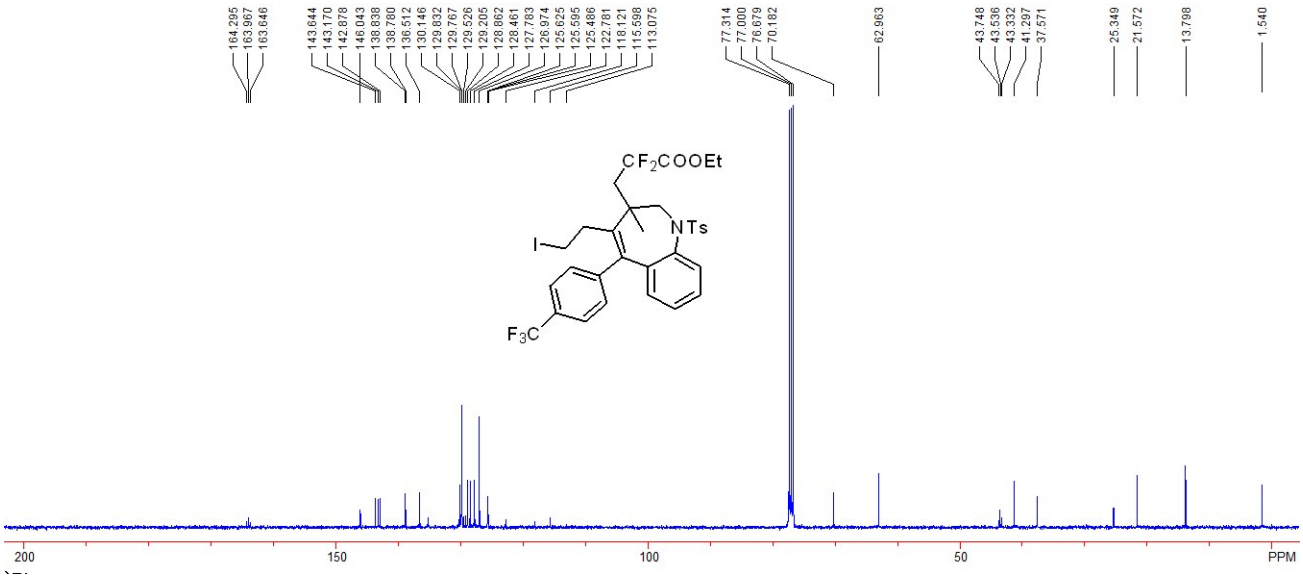

164.295
163.967
163.646
143.585
143.053
142.812
141.274
138.889
138.838
136.439
131.794
131.079
130.204
129.796
128.760
128.308
127.754
126.981
121.417
118.121
115.598
113.016
77.314
77.000
76.679
70.175
62.919
43.682
43.478
43.266
41.225
37.549
25.357
21.572
13.791
1.796
CF2COOEt
NTs
I
Br
200
150
100
50
0
PPM

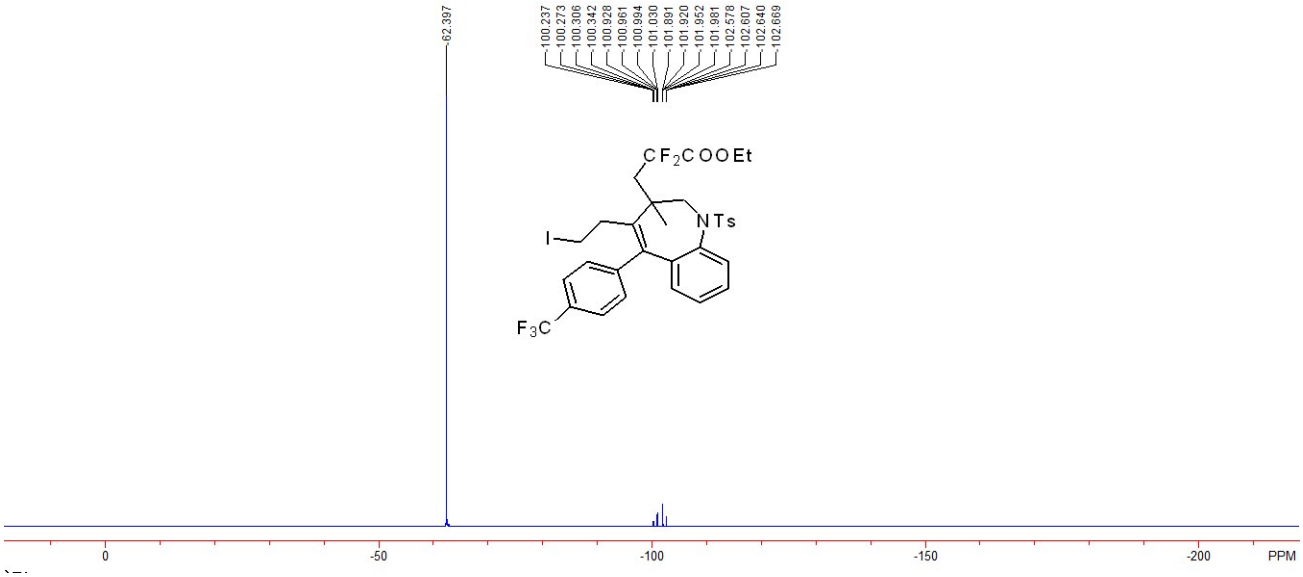

100.270
100.961
101.952
102.640
CF2COOEt
NTs
I
Br
0
-50
-100
-150
-200
PPM

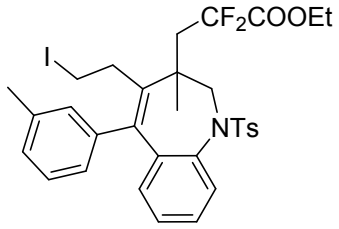



**Compound 2m**: 68 mg, 61%, A white solid, m.p. 126-128 $^{o}$C; IR ($CH_2Cl_2$): ν 2981, 2926, 2856, 1766, 1488, 1447, 1341, 1167, 1126, 1066, 1019, 862, 849, 775, 658 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.25 (t, 3H, $J$ = 7.2 Hz), 1.38 (s, 3H), 1.61-1.74 (m, 1H), 2.13-2.26 (m, 1H), 2.47 (s, 3H), 2.63-2.70 (m, 1H), 2.85-3.12 (m, 3H), 3.68 (d, 1H, $J$ = 13.6 Hz), 4.16-4.21 (m, 2H), 4.56 (d, 1H, $J$ = 13.6 Hz), 6.70 (d, 1H, $J$ = 7.2 Hz), 6.93 (dd, 1H, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz), 7.12-7.19 (m, 2H), 7.34 (d, 2H, $J$ = 8.0 Hz), 7.39 (d, 2H, $J$ = 8.0 Hz), 7.63 (d, 2H, $J$ = 8.0 Hz), 7.71 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 1.5, 13.8, 21.6, 25.3, 37.6, 41.3, 43.5 (t, $J_{C\text{-}F}$ = 21.2 Hz), 63.0, 70.2, 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 124.1 (q, $J_{C\text{-}F}$ = 270.5 Hz), 125.6 (q, $J_{C\text{-}F}$ = 3.0 Hz), 127.0, 127.8, 128.5, 128.9, 129.4 (q, $J_{C\text{-}F}$ = 32.1 Hz), 129.77, 129.83, 130.1, 136.5, 138.78, 138.84, 142.9, 143.2, 143.6, 146.0, 164.0 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.4 (s, 3F), -100.7 (ddd, 1F, $J_1$ = 259.8 Hz, $J_2$ = 25.9 Hz, $J_3$ = 13.5 Hz), -102.3 (ddd, 1F, $J_1$ = 259.8 Hz, $J_2$ = 23.3 Hz, $J_3$ = 10.9 Hz); MS (ESI) *m/z*: 765.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{32}H_{35}F_5IN_2O_4S^+$ requires: 765.1277, Found: 765.1275.



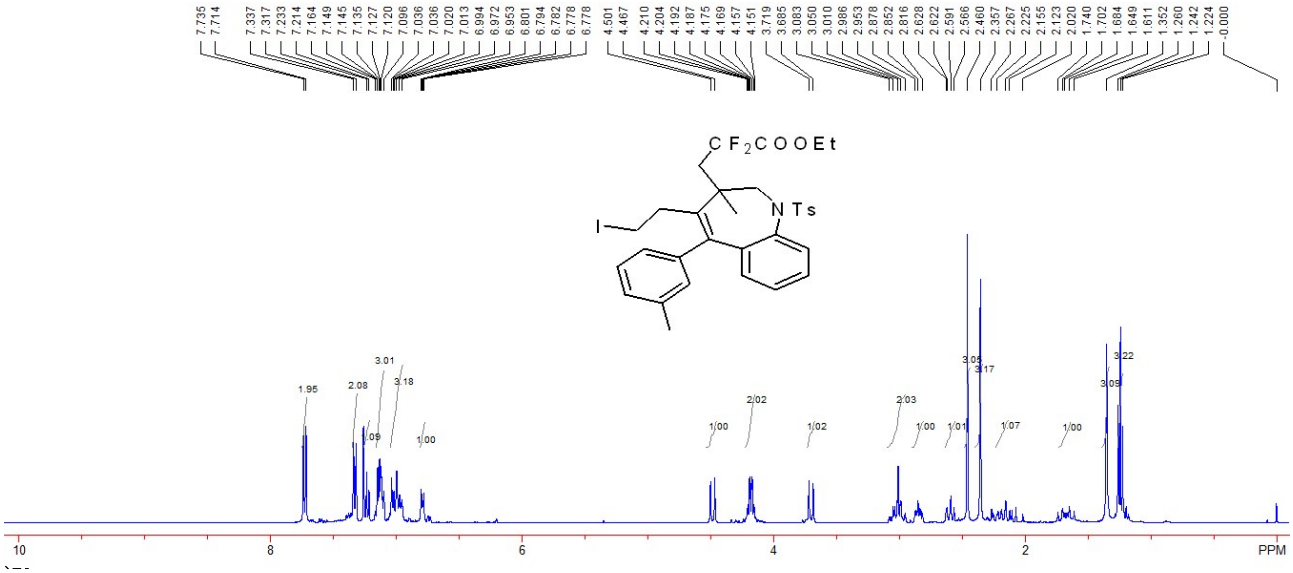


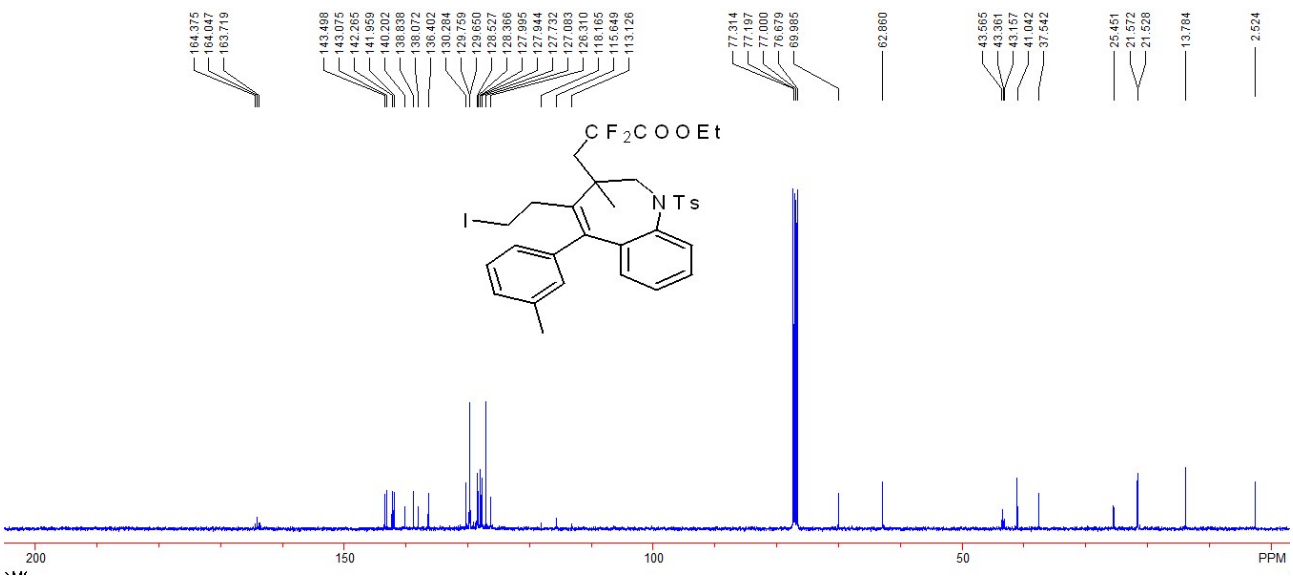



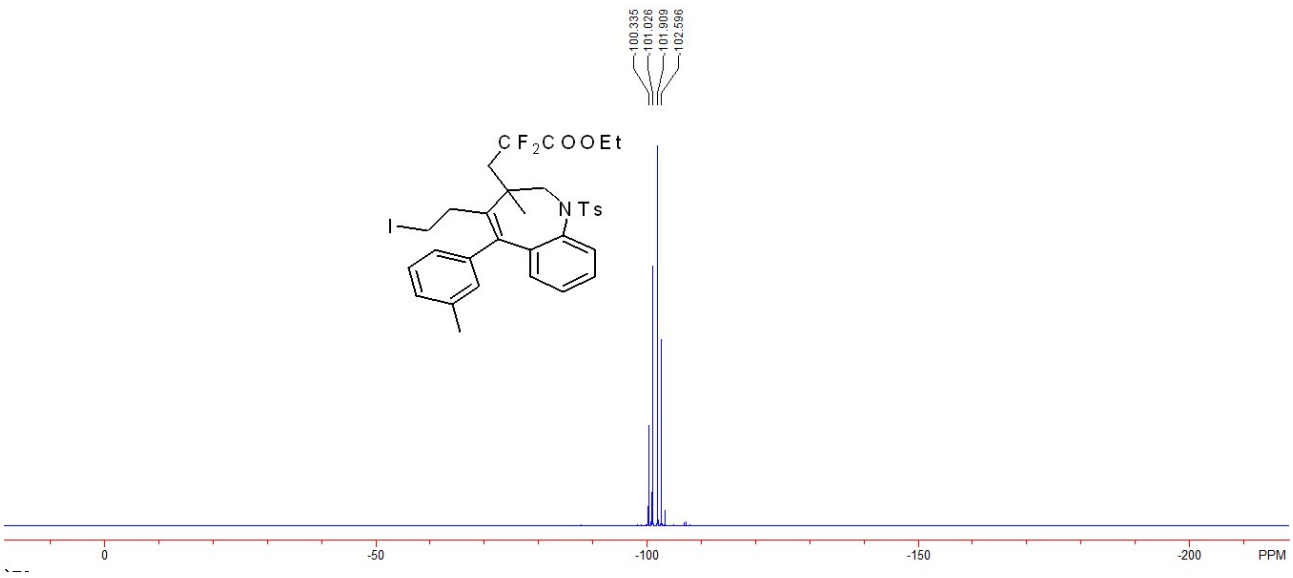



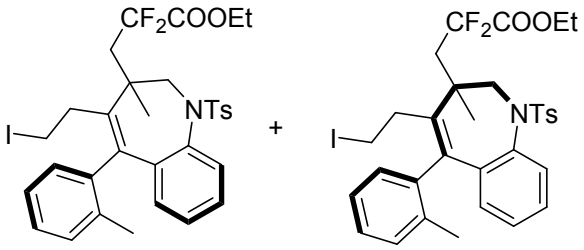

**Compound 2n**: 74 mg, 71%, A white solid, m.p. 134-136 $^{o}$C; IR ($CH_2Cl_2$): ν 3065, 2979, 2923, 2854, 1764, 1598, 1487, 1448, 1343, 1303, 1157, 1139, 1091, 1079, 1054, 1038, 859, 814, 733, 658 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.35 (s, 3H), 1.61-1.74 (m, 1H), 2.07-2.22 (m, 1H), 2.36 (s, 3H), 2.46 (s, 3H), 2.57-2.63 (m, 1H), 2.82-2.88 (m, 1H), 2.95-3.08 (m, 2H), 3.70 (d, 1H, $J$ = 13.6 Hz), 4.18 (qd, 2H, $J_1$ = 7.2 Hz, $J_2$ = 2.4 Hz), 4.48 (d, 1H, $J$ = 13.6 Hz), 6.78-6.80 (m, 1H), 6.95-7.04 (m, 3H), 7.10-7.16 (m, 3H), 7.21-7.25 (m, 1H), 7.33 (d, 2H, $J$ = 8.0 Hz), 7.72 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.5, 13.8, 21.5, 21.6, 25.5, 37.5,

41.0, 43.4 (t, $J_{C\text{-}F}$ = 20.4 Hz), 62.9, 70.0, 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 126.3, 127.1, 127.7, 127.9, 128.0, 128.4, 128.5, 129.7, 129.8, 130.3, 136.4, 138.1, 138.8, 140.2, 142.0, 143.1, 143.5, 164.0 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.7 (d, 1F, $J$ = 259.8 Hz), -102.3 (d, 1F, $J$ = 259.8 Hz); MS (ESI) *m/z*: 694.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{32}H_{35}F_2INO_4S^+$ requires: 694.1294, Found: 694.1292.

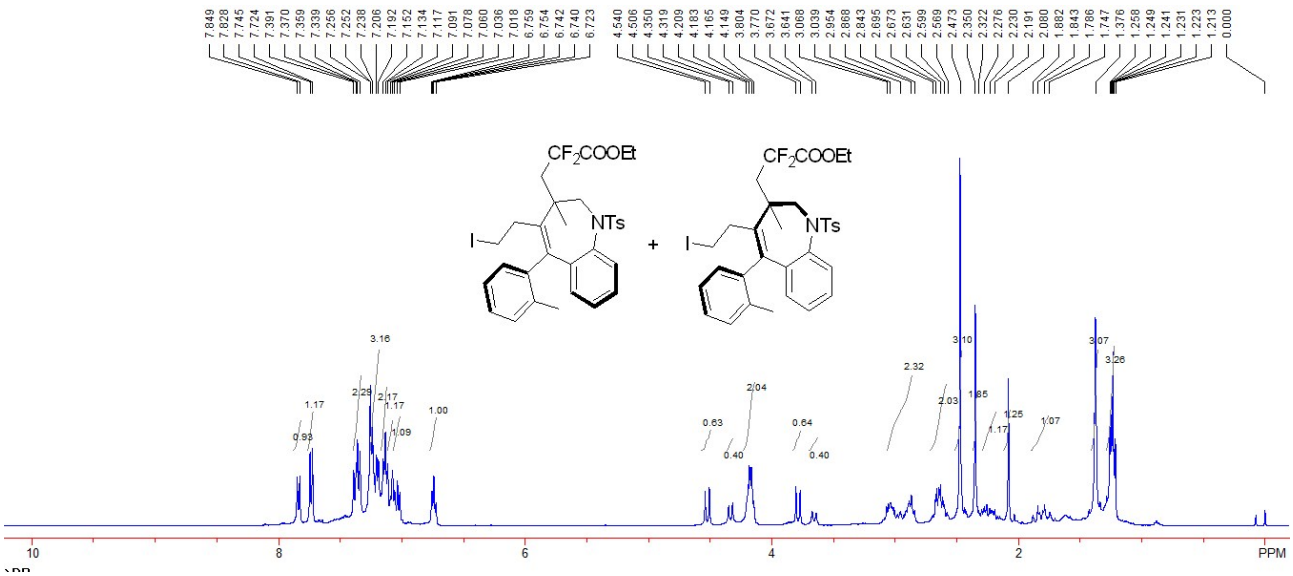


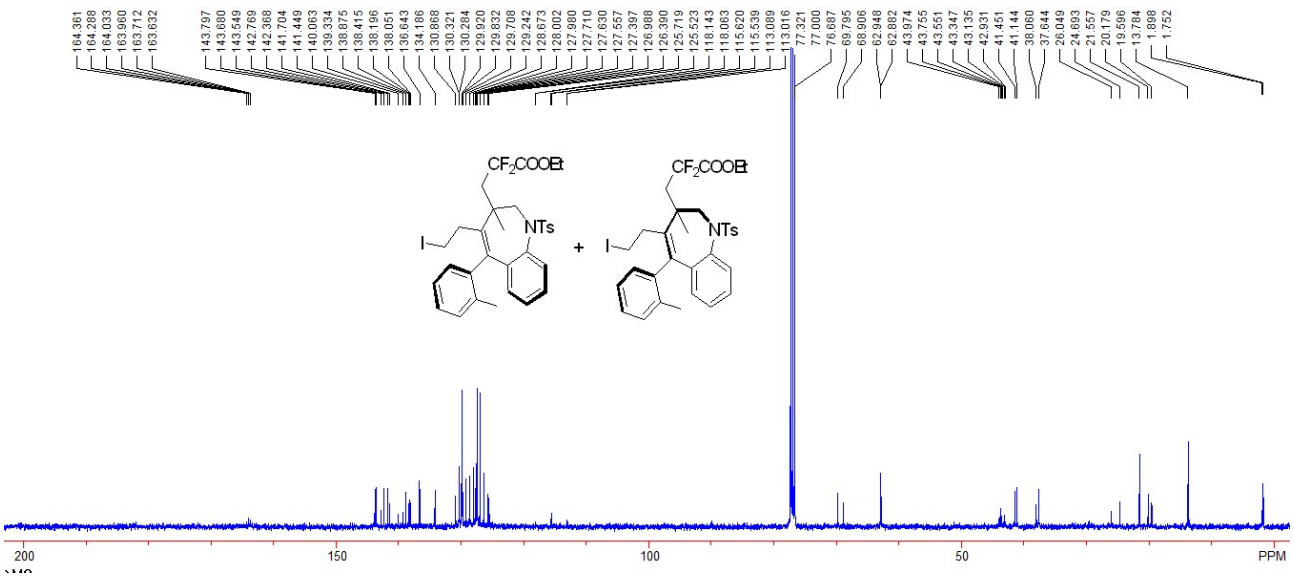



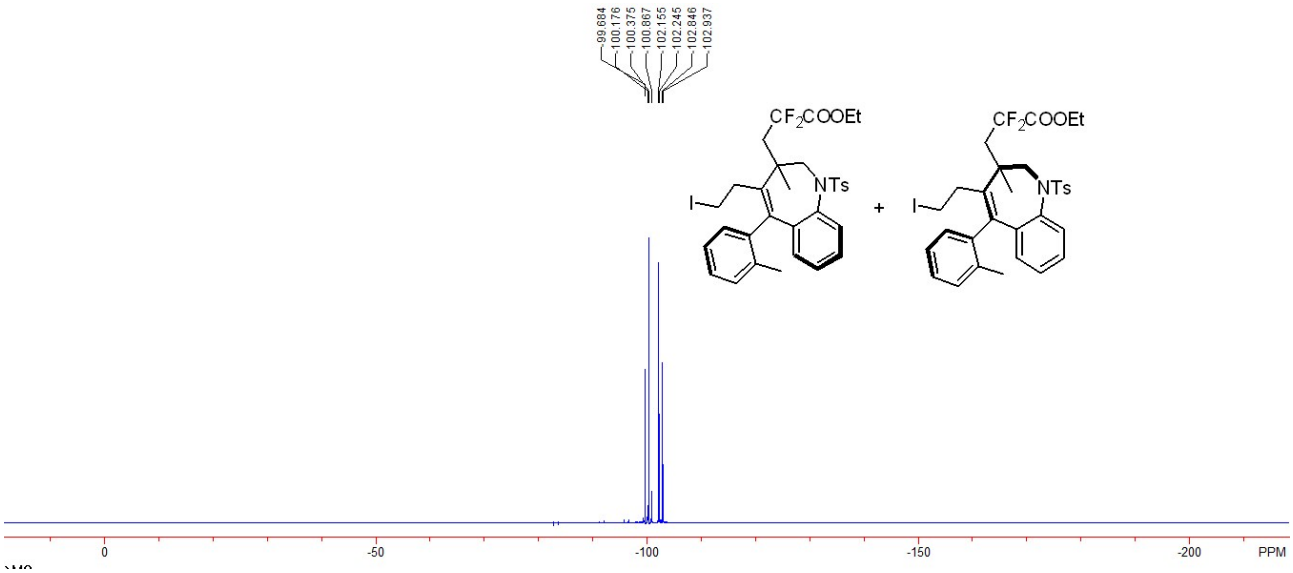


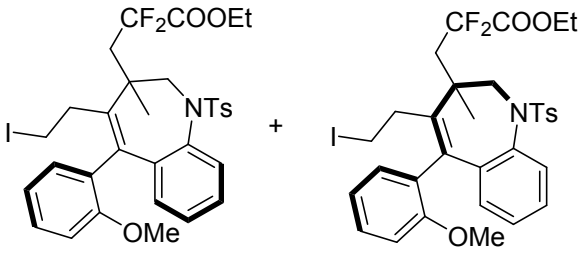




**Compound 2o**: 79 mg, 76%, dr = 3:2, inseparable, A colorlss oil; IR ($CH_2Cl_2$): ν 3062, 2974, 2925, 2856, 1765, 1597, 1486, 1447, 1343, 1303, 1191, 1156, 1142, 1112, 1091, 1047, 881, 815, 737, 658 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.21-1.26 (m, 3H), 1.38 (s, 3H), 1.75-1.88 (m, 1H), 2.08 (s, 1.2H), 2.19-2.30 (m, 1H), 2.35 (s, 1.8H), 2.47 (s, 3H), 2.57-2.67 (m, 2H), 2.84-3.07 (m, 2H), 3.66 (d, 0.4H, $J$ = 12.4 Hz), 3.79 (d, 0.6H, $J$ = 13.6 Hz), 4.15-4.21 (m, 2H), 4.33 (d, 0.4H, $J$ = 12.4 Hz), 4.52 (d, 0.6H, $J$ = 13.6 Hz), 6.72-6.76 (m, 1H), 7.03 (d, 1H, $J$ = 7.2 Hz), 7.08 (t, 1H, $J$ = 7.2 Hz), 7.13 (t, 2H, $J$ = 7.2 Hz), 7.19-7.26 (m, 3H), 7.34-7.39 (m, 2H), 7.73 (d, 1H, $J$ = 8.4 Hz), 7.84 (d, 1H, $J$ = 8.4 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 1.8, 1.9, 13.8, 19.6, 20.2, 21.6, 24.7, 26.0, 37.6, 38.1, 41.1, 41.5, 43.1 (t, $J_{C\text{-}F}$ = 21.2 Hz), 43.8 (t, $J_{C\text{-}F}$ = 21.9 Hz), 62.88, 62.95, 68.9, 69.8, 115.5 (t, $J_{C\text{-}F}$ = 252.4 Hz), 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 125.5, 125.7, 126.4, 127.0, 127.4, 127.56, 127.63, 127.7, 127.98, 128.00, 128.7, 129.2, 129.7, 129.8, 129.9, 130.28, 130.32, 130.9, 134.2, 136.6, 138.1, 138.2, 138.4, 138.9, 139.3, 140.1, 141.4, 141.7, 142.4, 142.8, 143.5, 143.7, 143.8, 163.96 (t, $J_{C\text{-}F}$ = 32.8 Hz), 164.36 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.0 (d, 0.6F, $J$ = 259.8 Hz), -100.5 (d, 0.4F, $J$ = 259.8 Hz), -102.5 (d, 0.6F, $J$ = 259.8 Hz), -102.6 (d, 0.4F, $J$ = 259.8 Hz); MS (ESI) *m/z*: 711.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{32}H_{38}F_2IN_2O_4S^+$ requires: 711.1560, Found: 711.1558.

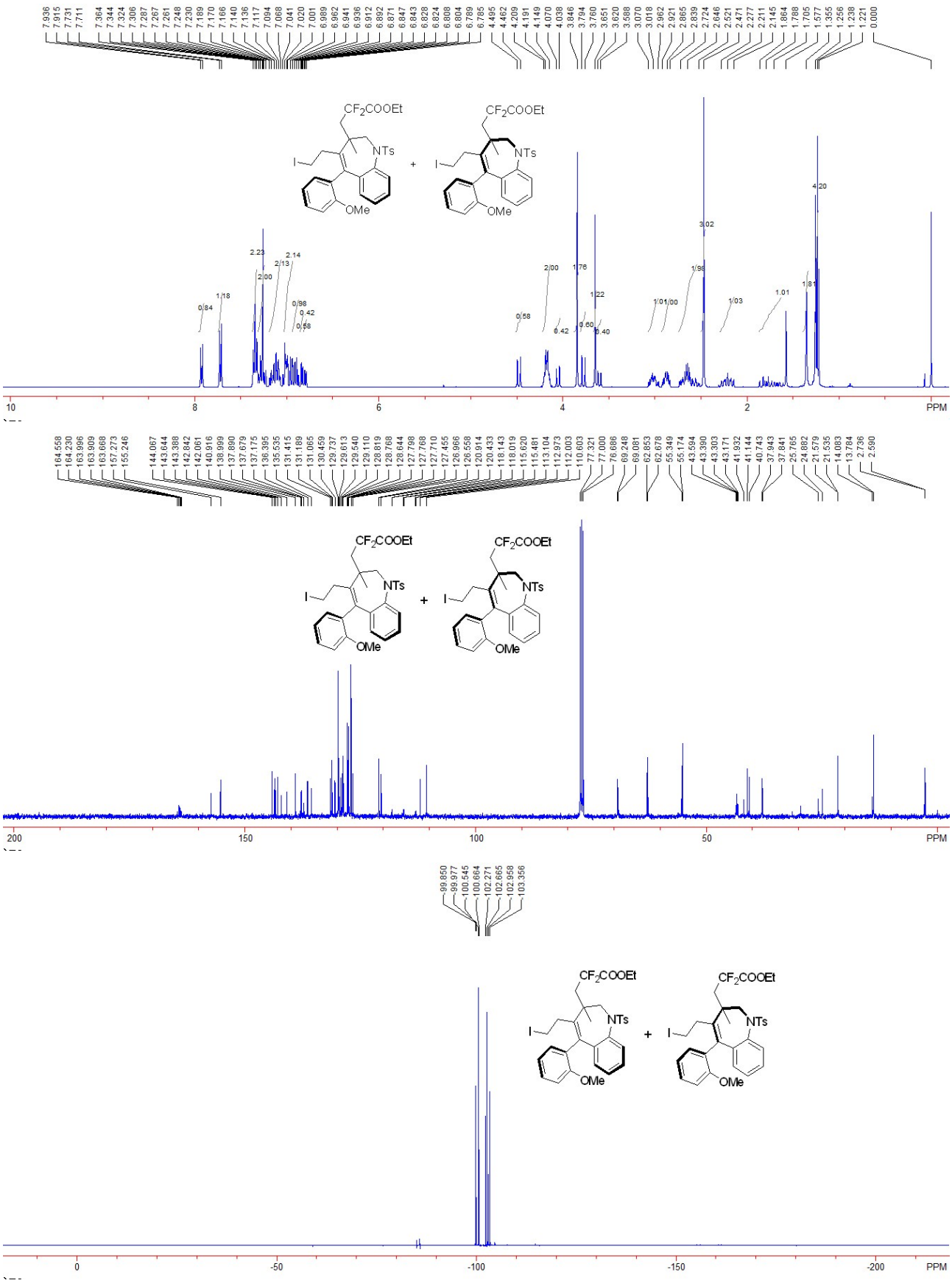

7.849 7.828 7.745 7.724 7.391 7.370 7.359 7.339 7.256 7.252 7.238 7.206 7.192 7.152 7.134 7.117 7.091 7.078 7.060 7.036 7.018 6.759 6.754 6.742 6.740 6.723
4.540 4.506 4.350 4.319 4.209 4.183 4.165 4.149 3.804 3.770 3.672 3.641 3.068 3.039 2.954 2.868 2.843 2.695 2.673 2.631 2.599 2.569 2.473 2.350 2.322 2.276 2.230 2.191 2.080 1.882 1.843 1.786 1.747 1.376 1.258 1.249 1.241 1.231 1.223 1.213 0.000
CF2COOEt
NTs
I
+
3.16
2.28
2.17
1.17
1.17
1.09
1.00
0.93
2.04
0.63
0.40
0.64
0.40
2.32
2.03
3.10
1.85
1.25
1.17
1.07
3.07
3.26
10
8
6
4
2
PPM

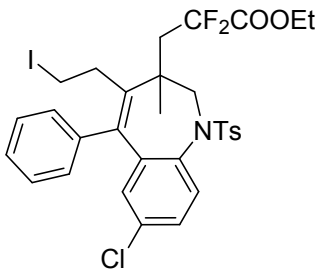

164.361 164.288 164.033 163.960 163.712 163.632
143.797 143.680 143.549 142.769 142.368 141.704 141.449 140.063 139.334 138.875 138.415 138.196 138.051 136.643 134.186 130.868 130.321 130.284 129.920 129.832 129.708 129.242 128.673 128.002 127.980 127.710 127.630 127.557 127.397 126.988 126.390 125.719 125.523 118.143 118.063 115.620 115.539 113.089 113.016
77.321 77.000 76.687 69.795 68.906 62.948 62.882 43.974 43.755 43.551 43.347 43.135 42.931 41.451 41.144 38.060 37.644 26.049 24.693 21.557 20.179 19.596 13.784 1.898 1.752
CF2COOEt
NTs
I
+
200
150
100
50
PPM


99.684 100.176 100.375 100.867 102.155 102.245 102.846 102.937
CF2COOEt
NTs
I
+
0
-50
-100
-150
-200
PPM

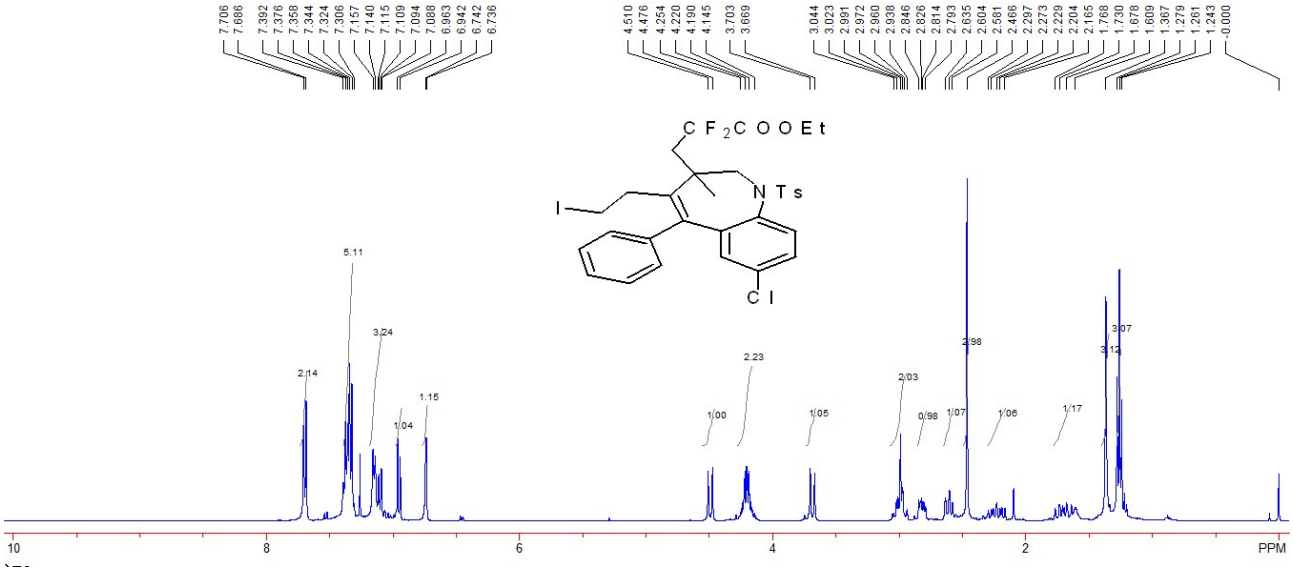


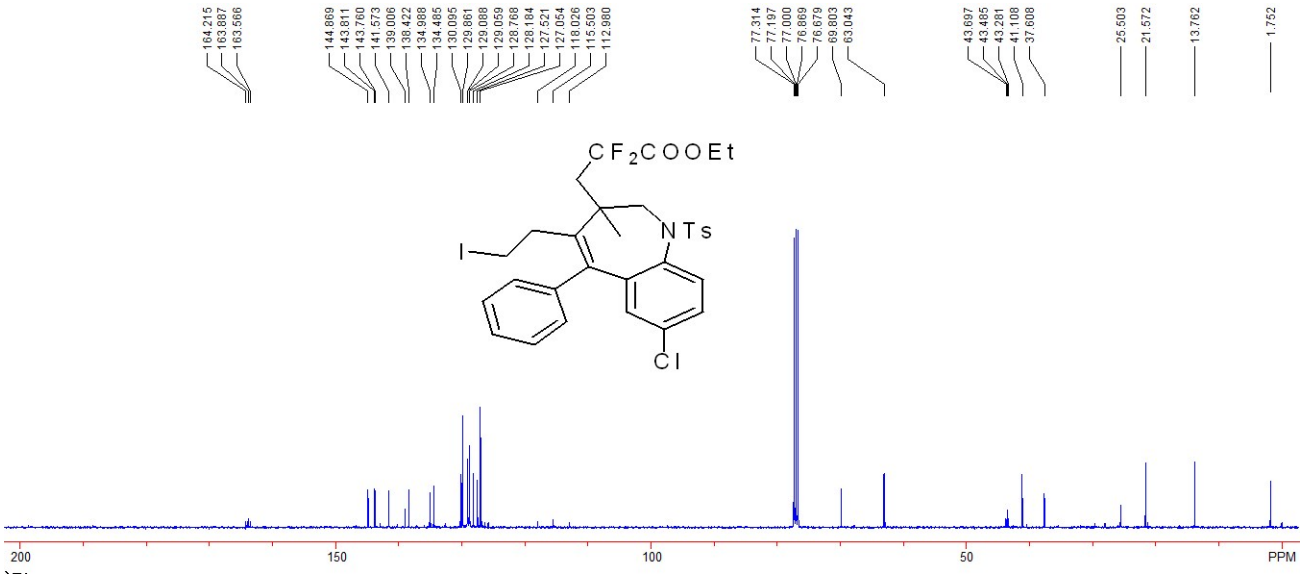

**Compound 2p**: 90 mg, 85%, dr = 3:2, inseparable, A colorless oil; IR ($CH_2Cl_2$): ν 3065, 2973, 2926, 2851, 1764, 1596, 1488, 1456, 1340, 1303, 1194, 1155, 1091, 1048, 1026, 862, 729, 658 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.26 (s, 1.2H), 1.36 (s, 1.8H), 1.64-1.86 (m, 1H), 2.15-2.28 (m, 1H), 2.47 (s, 3H), 2.53-2.73 (m, 2H), 2.84-2.92 (m, 1H), 2.96-3.07 (m, 1H), 3.60 (d, 0.4H, $J$ = 12.8 Hz), 3.65 (s, 1.2H), 3.78 (d, 0.6H, $J$ = 13.6 Hz), 3.85 (s, 1.8H), 4.05 (d, 0.4H, $J$ = 12.8 Hz), 4.14-4.21 (m, 2H), 4.48 (d, 0.6H, $J$ = 13.6 Hz), 6.80 (dd, 0.4H, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz), 6.84 (dd, 0.6H, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz), 6.87-6.94 (m, 1H), 6.96-7.04 (m, 2H), 7.07-7.12 (m, 2H), 7.17-7.31 (m, 2H), 7.34 (t, 2H, $J$ = 8.0 Hz), 7.72 (d, 1H, $J$ = 8.0 Hz), 7.93 (d, 1H, $J$ = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.6, 2.7, 13.8, 14.1, 21.5, 21.6, 24.9, 25.8, 37.8, 37.9, 40.7, 41.1, 43.3 (t, $J_{C\text{-}F}$ = 20.5 Hz), 43.4 (t, $J_{C\text{-}F}$ = 20.4 Hz), 55.2, 55.3, 62.7, 62.9, 69.1, 69.2, 110.6, 112.0, 115.5 (t, $J_{C\text{-}F}$ = 253.8 Hz), 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 120.4, 120.9, 126.6, 127.0, 127.5, 127.7, 127.77, 127.80, 128.6, 128.77, 128.82, 129.1, 129.5, 129.6, 129.7, 130.5, 131.1, 131.2, 131.4, 135.5, 136.4, 137.2, 137.7, 137.9, 139.0, 140.9, 142.1, 142.8, 143.4, 143.6, 144.1, 155.2, 157.3, 164.0 (t, $J_{C\text{-}F}$ = 32.8 Hz), 164.2 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.2 (d, 0.6F, $J$ = 259.8 Hz), -100.3 (d, 0.4F, $J$ = 258.3 Hz), -102.6 (d, 0.4F, $J$ = 258.3 Hz), -103.0 (d, 0.6F, $J$ = 259.8 Hz); MS (ESI) *m/z*: 727.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{32}H_{38}F_2IN_2O_5S^+$ requires: 727.1509, Found: 727.1507.

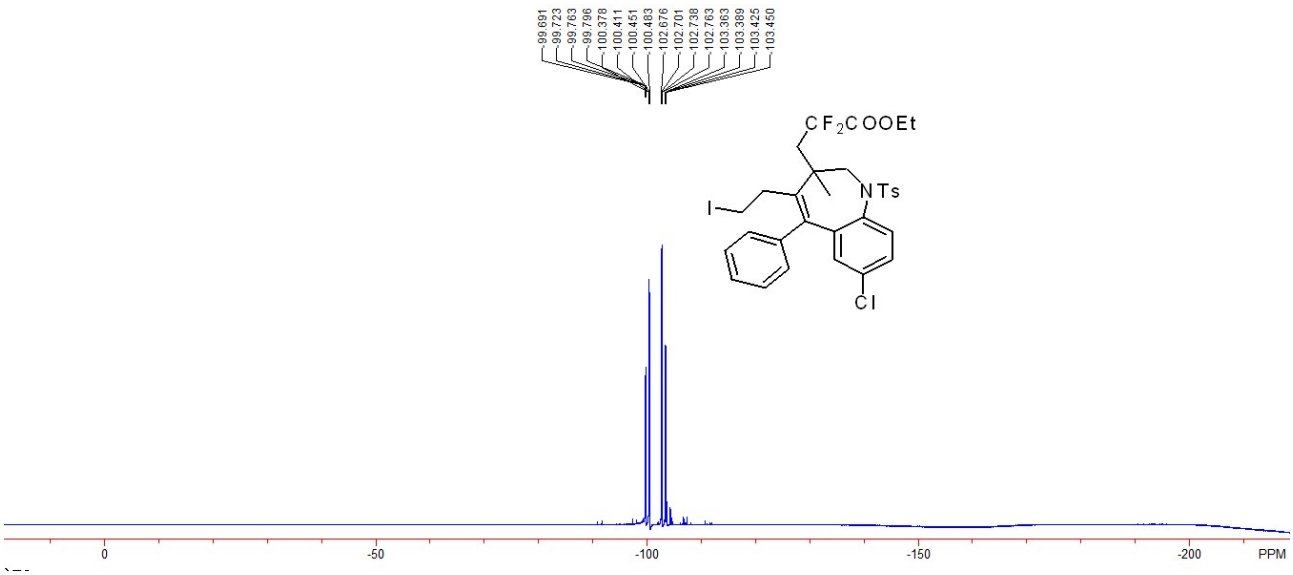

CF2COOEt
NTs
I
OMe
+
PPM

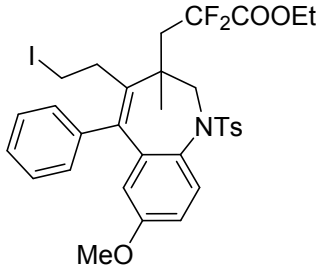



**Compound 2q**: 79 mg, 74%, A white solid, m.p. 140-142 $^{o}$C; IR ($CH_2Cl_2$): ν 2974, 2925, 2870, 1764, 1483, 1343, 1303, 1155, 1139, 1089, 1077, 1049, 880, 814, 705, 660 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.26 (t, 3H, $J$ = 7.2 Hz), 1.28 (s, 3H), 1.68-1.77 (m, 1H), 2.17-2.30 (m, 1H), 2.47 (s, 3H), 2.58-2.64 (m, 1H), 2.79-2.94 (m, 1H), 2.94-3.02 (m, 2H), 3.69 (d, 1H, $J$ = 13.6 Hz), 4.16-4.25 (m, 2H), 4.49 (d, 1H, $J$ = 13.6 Hz), 6.74 (d, 1H, $J$ = 2.4 Hz), 6.95 (d, 1H, $J$ = 8.4 Hz), 7.10 (dd, 1H, $J_1$ = 8.4 Hz, $J_2$ = 2.4 Hz), 7.15 (d, 2H, $J$ = 6.8 Hz), 7.31-7.39 (m, 5H), 7.70 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 1.8, 13.8, 21.6, 25.5, 37.6, 41.1, 43.5 (t, $J_{C-F}$ = 21.2 Hz), 63.0, 69.8, 115.5 (t, $J_{C-F}$ = 252.3 Hz), 127.1, 127.5, 128.2, 128.8, 129.06, 129.09, 129.9, 130.1, 134.5, 135.0, 138.4, 139.0, 141.6, 143.76, 143.81, 144.9, 163.9 (t, $J_{C-F}$ = 32.8 Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.1 (ddd, 1F, $J_1$ = 258.3 Hz, $J_2$ = 27.1 Hz, $J_3$ = 12.0 Hz), -103.1 (ddd, 1F, $J_1$ = 258.3 Hz, $J_2$ = 23.3 Hz, $J_3$ = 9.4 Hz); MS (ESI) *m/z*: 731.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{35}ClF_2IN_2O_4S^+$ requires: 731.1013, Found: 731.1010.



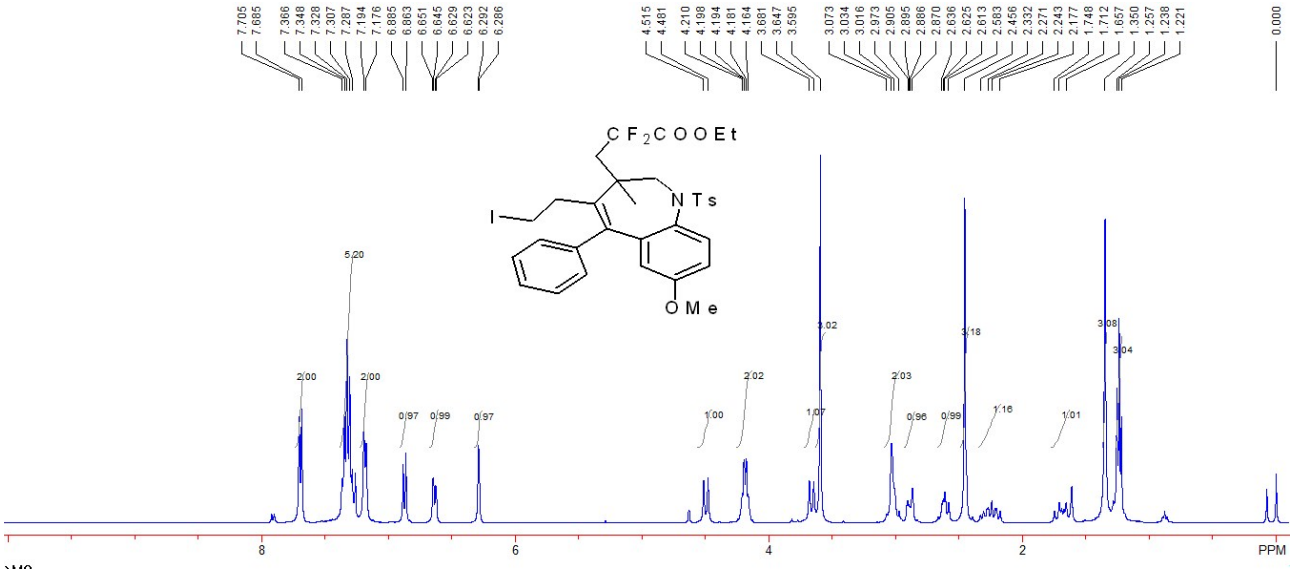


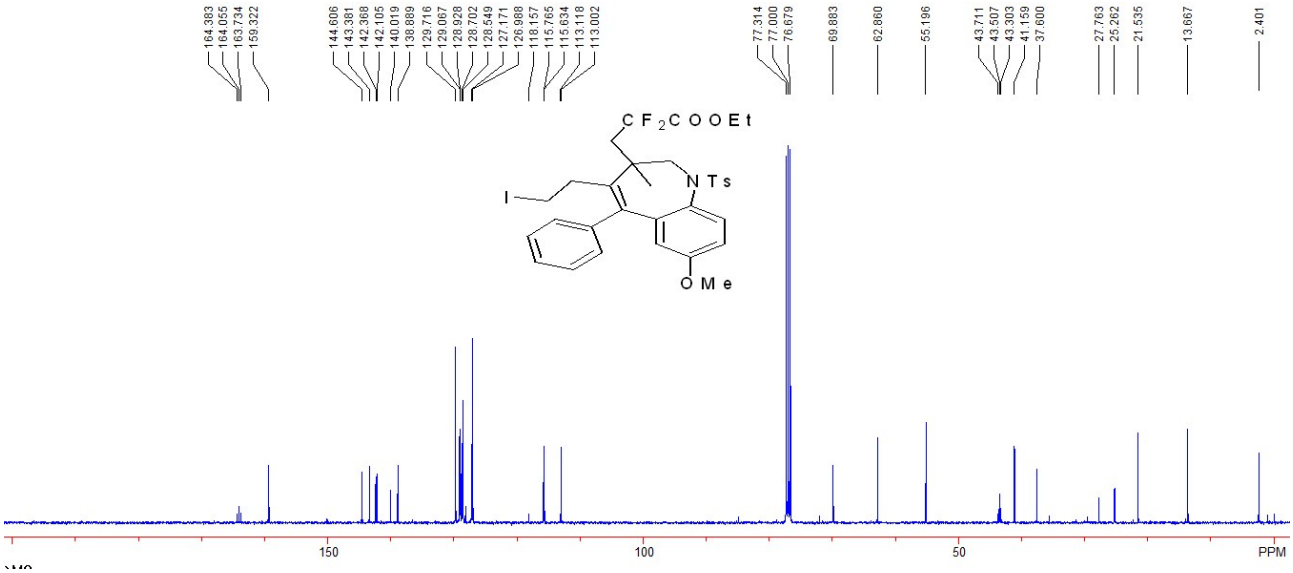



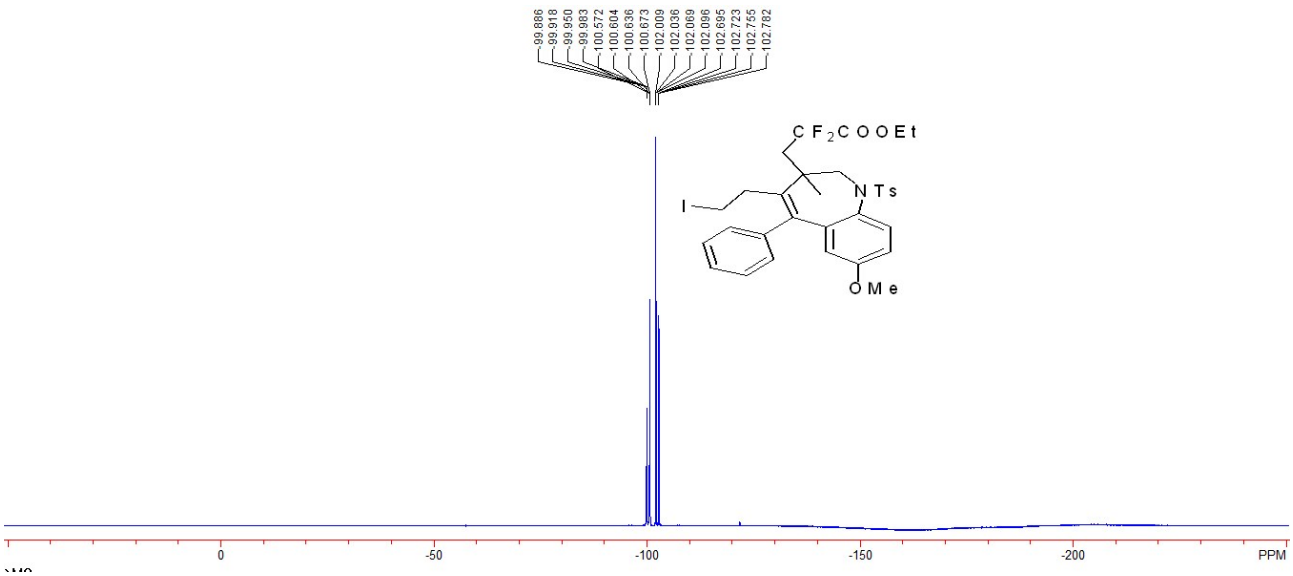



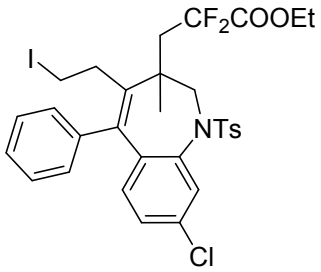

**Compound 2r**: 83 mg, 78%, A white solid, m.p. 129-131 $^{o}$C; IR ($CH_2Cl_2$): ν 2979, 2967, 2928, 2851, 1764, 1734, 1598, 1573, 1494, 1343, 1302, 1157, 1091, 1037, 878, 862, 814, 708, 658 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.35 (s, 3H), 1.66-1.75 (m, 1H), 2.18-2.33 (m, 1H), 2.46 (s, 3H), 2.58-2.64 (m, 1H), 2.87-2.91 (m, 1H), 2.97-3.07 (m, 2H), 3.60 (s, 3H), 3.66 (d, 1H, $J$ = 13.6 Hz), 4.16-4.21 (m, 2H), 4.50 (d, 1H, $J$ = 13.6 Hz), 6.29 (d, 1H, $J$ = 8.8 Hz), 6.64 (dd, 1H, $J_1$ = 8.4 Hz, $J_2$ = 2.4 Hz), 6.87 (d, 1H, $J$ = 8.8 Hz), 7.19 (d, 2H, $J$ = 7.2 Hz), 7.26-

7.37 (m, 5H), 7.70 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.4, 13.7, 21.5, 25.3, 37.6, 41.2, 43.5 (t, $J_{C\text{-}F}$ = 20.4 Hz), 55.2, 62.9, 69.9, 113.0, 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 115.8, 127.0, 127.2, 128.5, 128.7, 128.9, 129.1, 129.7, 138.9, 140.0, 142.1, 142.4, 143.4, 144.6, 159.3, 164.1 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.3 (d, 1F, $J$ = 258.7 Hz), -102.4 (d, 1F, $J$ = 258.7 Hz); MS (ESI) *m/z*: 727.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{32}H_{38}F_2IN_2O_5S^+$ requires: 727.1509, Found: 727.1508.

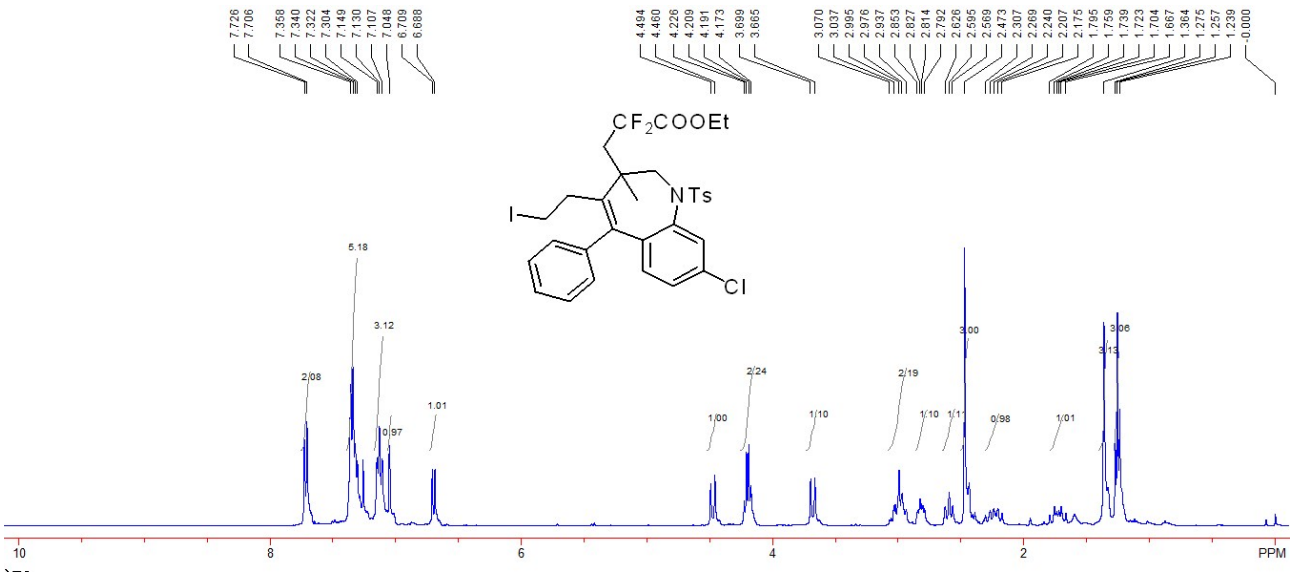


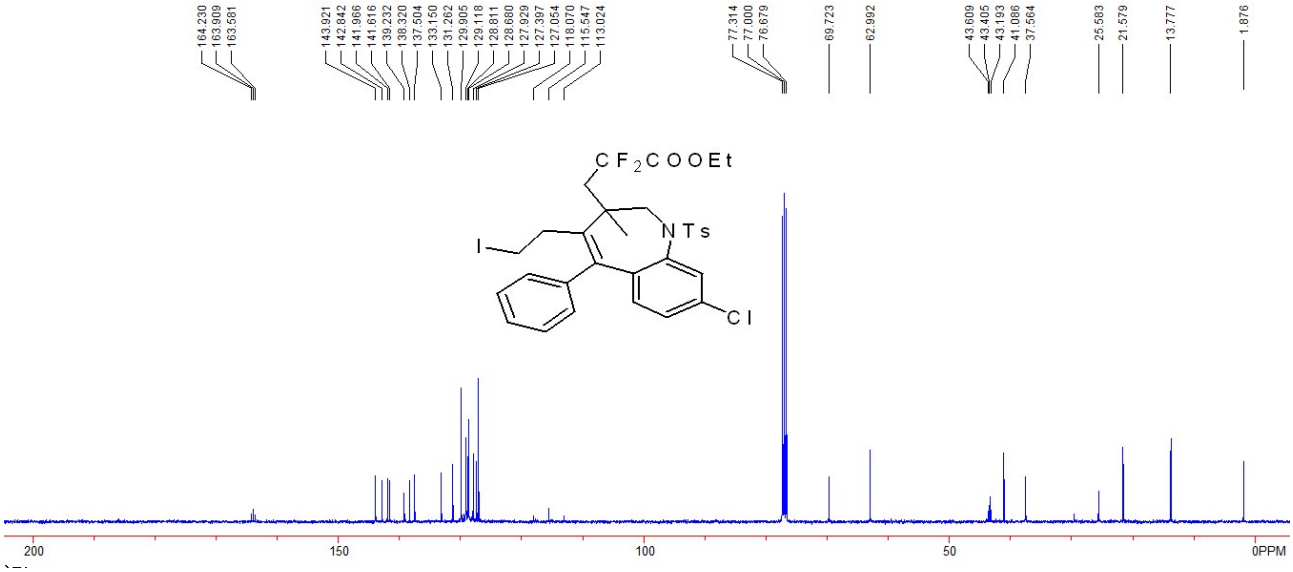



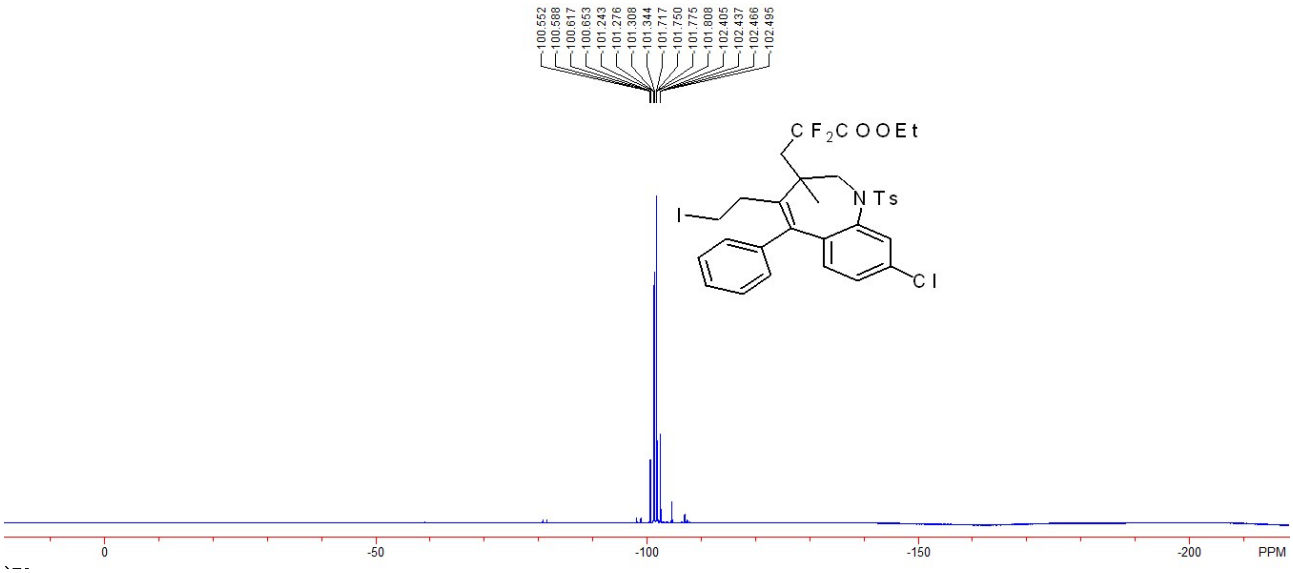


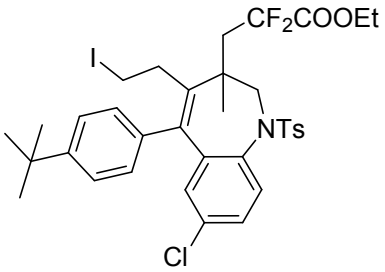




**Compound 2s**: 69 mg, 65%, A white solid, m.p. 134-136 $^{o}$C; IR ($CH_2Cl_2$): ν 2973, 2929, 2882, 1765, 1485, 1455, 1379, 1343, 1303, 1272, 1088, 1046, 880, 815, 709, 658 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.26 (t, 3H, $J$ = 7.2 Hz), 1.36 (s, 3H), 1.67-1.80 (m, 1H), 2.18-2.31 (m, 1H), 2.47 (s, 3H), 2.57-2.63 (m, 1H), 2.79-2.85 (m, 1H), 2.94-3.07 (m, 2H), 3.68 (d, 1H, $J$ = 13.6 Hz), 4.17-4.23 (m, 2H), 4.48 (d, 1H, $J$ = 13.6 Hz), 6.70 (d, 1H, $J$ = 8.4 Hz), 7.05 (s, 1H), 7.11-7.15 (m, 3H), 7.30-7.36 (m, 5H), 7.72 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 1.9, 13.8, 21.6, 25.6, 37.6, 41.1, 43.4 (t, $J_{C\text{-}F}$ = 21.2 Hz), 63.0, 69.7, 115.5 (t, $J_{C\text{-}F}$ = 252.3 Hz), 127.1, 127.4, 127.9, 128.7, 128.8, 129.1, 129.9, 131.3, 133.2, 137.5, 138.3, 139.2, 141.6, 142.0, 142.8, 143.9, 163.9 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -101.0 (ddd, 1F, $J_1$ = 259.8 Hz, $J_2$ = 24.4 Hz, $J_3$ = 13.5 Hz), -102.1 (ddd, 1F, $J_1$ = 259.8 Hz, $J_2$ = 21.8 Hz, $J_3$ = 10.9 Hz); MS (ESI) *m/z*: 714.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{32}ClF_2INO_4S^+$ requires: 714.0748, Found: 714.0771.

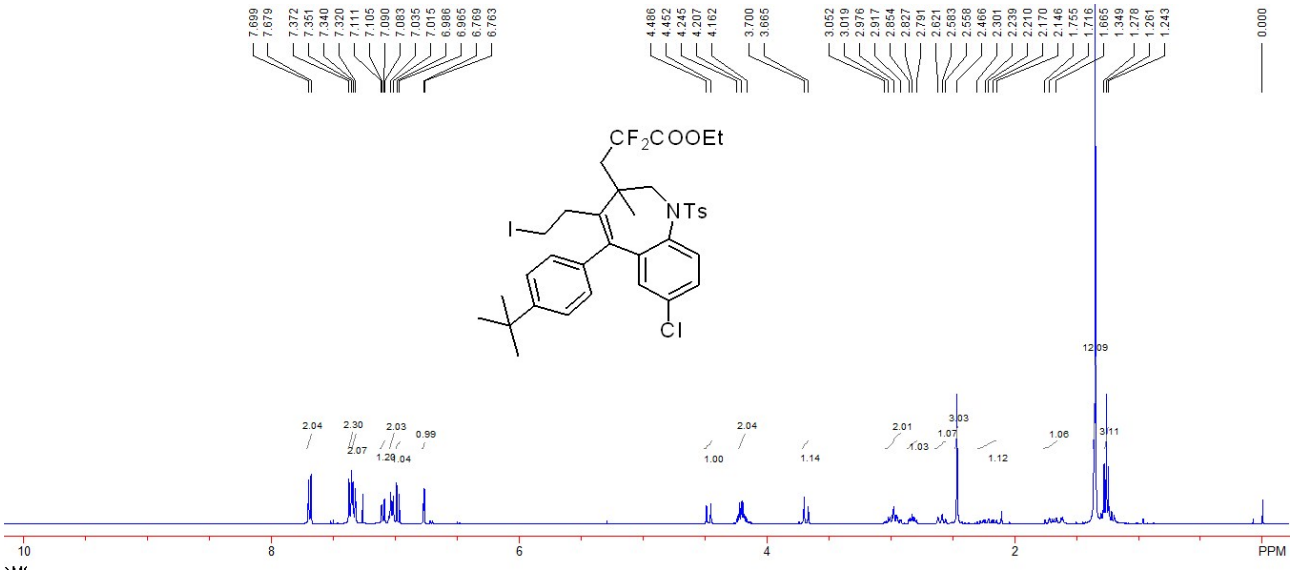

7.726
7.706
7.358
7.340
7.322
7.304
7.149
7.130
7.107
7.048
6.709
6.688
4.494
4.460
4.226
4.209
4.191
4.173
3.699
3.665
3.070
3.037
2.995
2.976
2.937
2.853
2.827
2.814
2.792
2.626
2.595
2.569
2.473
2.307
2.269
2.240
2.207
2.175
1.795
1.759
1.739
1.723
1.704
1.667
1.364
1.275
1.257
1.239
-0.000
CF2COOEt
NTs
I
Cl
5.18
3.12
2.08
1.01
0.97
1.00
2.24
1.10
2.19
1.10
3.00
0.98
1.01
3.06
10
8
6
4
2
PPM

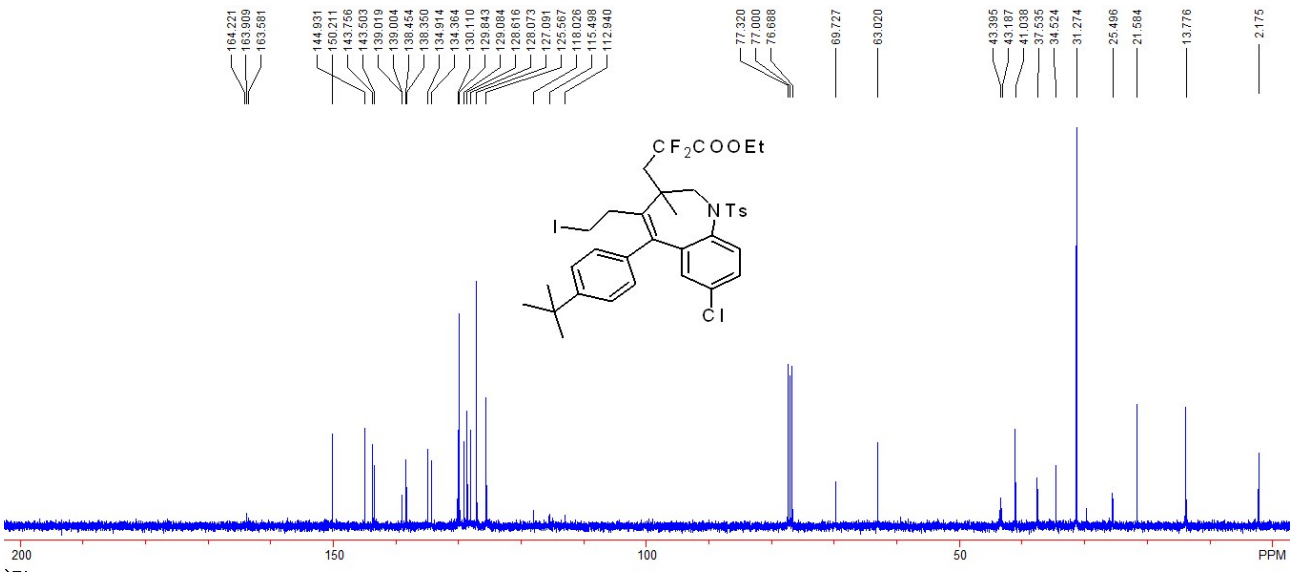

164.230
163.909
163.581
143.921
142.842
141.986
141.616
139.232
138.320
137.504
133.150
131.262
129.905
129.118
128.811
128.680
127.929
127.397
127.054
118.070
115.547
113.024
77.314
77.000
76.679
69.723
62.992
43.609
43.405
43.193
41.086
37.564
25.583
21.579
13.777
1.876
CF2COOEt
NTs
I
Cl
200
150
100
50
0PPM

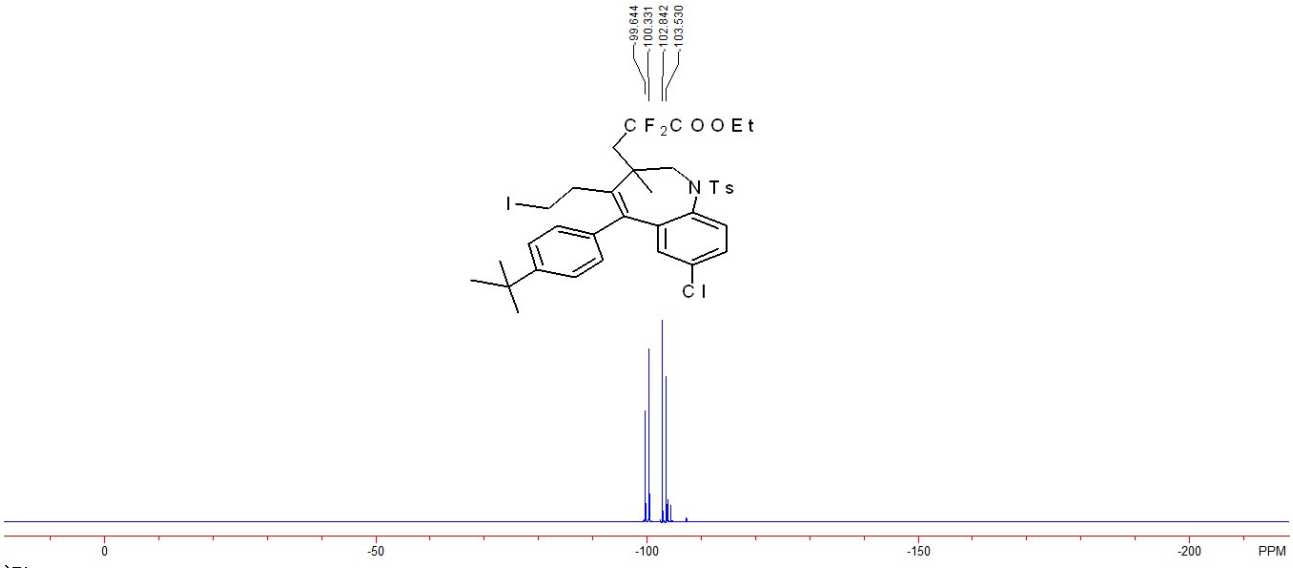

100.552
100.588
100.617
100.653
101.243
101.276
101.308
101.344
101.717
101.750
101.775
101.808
102.405
102.437
102.466
102.495
CF2COOEt
NTs
I
Cl
0
-50
-100
-150
-200
PPM

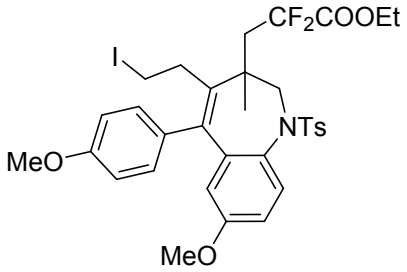



**Compound 2t**: 86 mg, 74%, A white solid, m.p. 149-151 °C; IR ($CH_2Cl_2$): ν 2969, 2903, 2868, 1766, 1484, 1344, 1156, 1140, 1090, 1046, 880, 815, 766, 661 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.26 (t, 3H, $J$ = 7.2 Hz), 1.35 (s, 12H), 1.61-1.76 (m, 1H), 2.15-2.30 (m, 1H), 2.47 (s, 3H), 2.56-2.62 (m, 1H), 2.79-2.85 (m, 1H), 2.92-3.05 (m, 2H), 3.68 (d, 1H, $J$ = 13.6 Hz), 4.16-4.25 (m, 2H), 4.47 (d, 1H, $J$ = 13.6 Hz), 6.77 (d, 1H, $J$ = 2.4 Hz), 6.98 (d, 1H, $J$ = 8.4 Hz), 7.03 (d, 2H, $J$ = 8.0 Hz), 7.10 (dd, 1H, $J_1$ = 8.4 Hz, $J_2$ = 2.4 Hz), 7.33 (d, 2H, $J$ = 8.0 Hz), 7.36 (d, 2H, $J$ = 8.4 Hz), 7.69 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.2, 13.8, 21.6, 25.5, 31.3, 34.5, 37.5, 41.0, 43.4 (t, $J_{C\text{-}F}$ = 21.2 Hz), 63.0, 69.7, 115.5 (t, $J_{C\text{-}F}$ = 253.0 Hz), 125.6, 127.1, 128.1, 128.6, 129.1, 129.8, 130.1, 134.4, 134.9, 138.4, 138.5, 139.0, 143.5, 143.8, 144.9, 150.2, 163.9 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.0 (d, 1F, $J$ = 258.3 Hz), -103.2 (d, 1F, $J$ = 258.3 Hz); MS (ESI) *m/z*: 787.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{35}H_{43}ClF_2IN_2O_4S^+$ requires: 787.1639, Found: 787.1639.



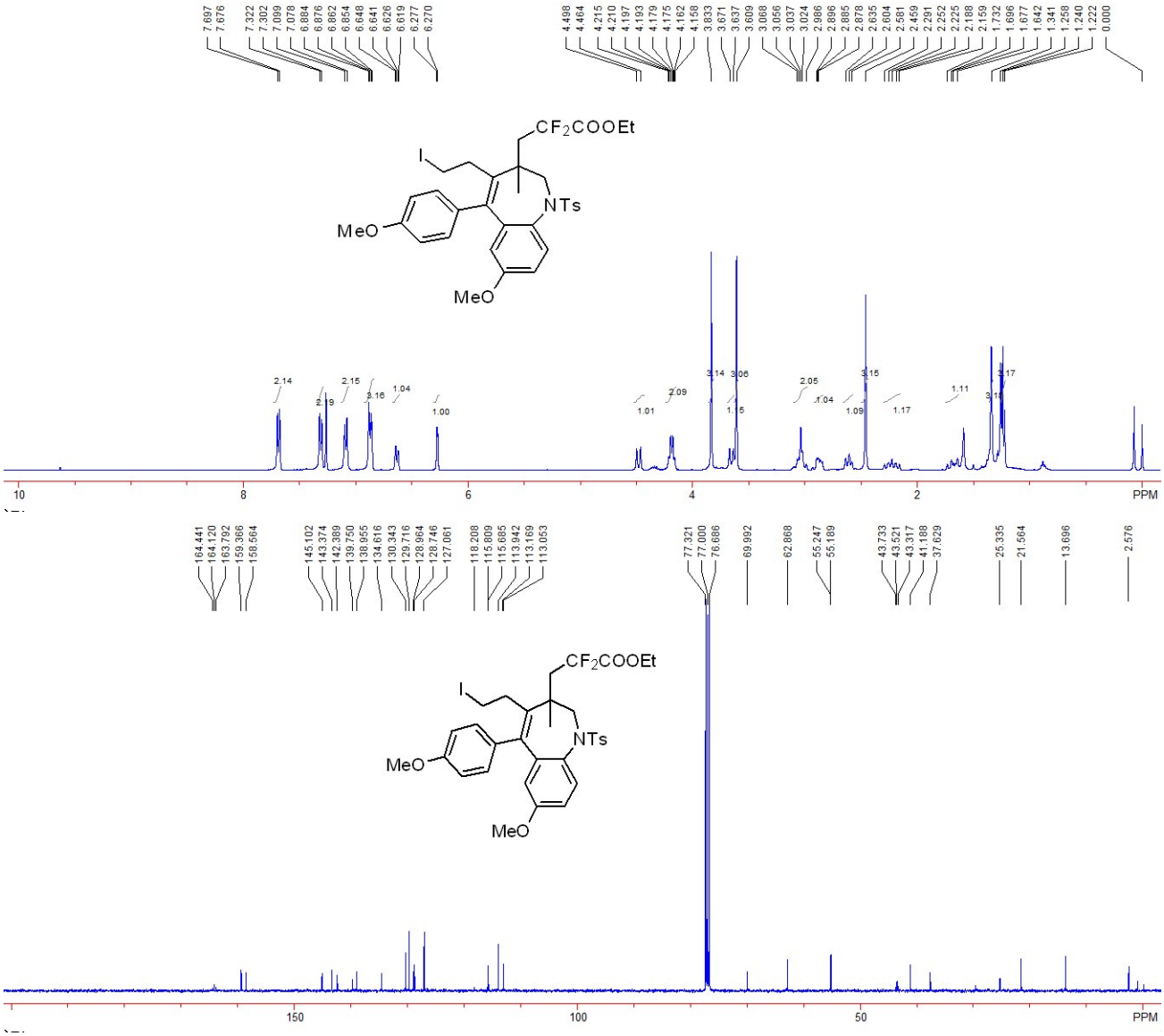


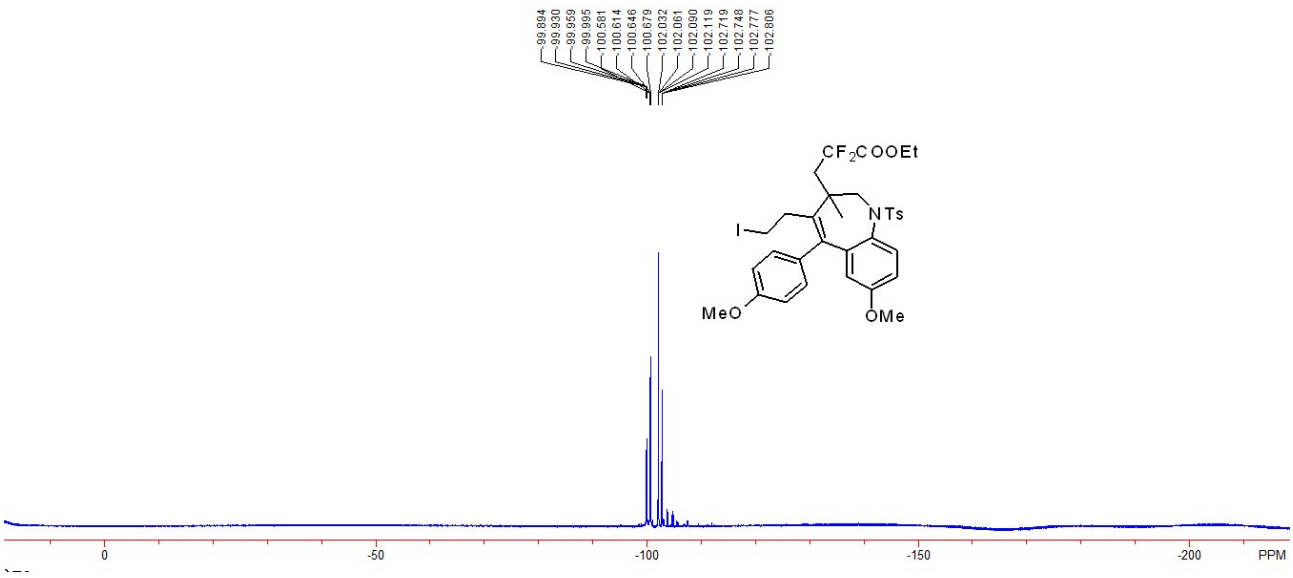



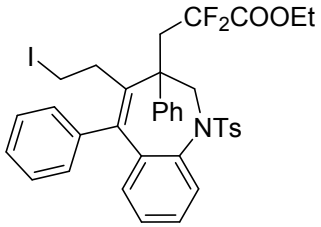




**Compound 2u**: 74 mg, 67%, A white solid, m.p. 139-141 $^{o}$C; IR ($CH_2Cl_2$): ν 2974, 2929, 2856, 1764, 1734, 1605, 1508, 1494, 1465, 1341, 1302, 1287, 1245, 1156, 1141, 1091, 1035, 879, 711, 655 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, 3H, $J$ = 7.2 Hz), 1.34 (s, 3H), 1.68-1.73 (m, 1H), 2.16-2.29 (m, 1H), 2.46 (s, 3H), 2.58-2.64 (m, 1H), 2.88-2.90 (m, 1H), 2.99-3.07 (m, 2H), 3.61 (s, 3H), 3.65 (d, 1H, $J$ = 13.6 Hz), 3.83 (s, 3H), 4.19 (qd, 2H, $J_1$ = 7.2 Hz, $J_2$ = 1.6 Hz), 4.48 (d, 1H, $J$ = 13.6 Hz), 6.28 (d, 1H, $J$ = 2.8 Hz), 6.63 (dd, 1H, $J_1$ = 8.8 Hz, $J_2$ = 2.8 Hz), 6.87 (dd, 3H, $J_1$ = 8.8

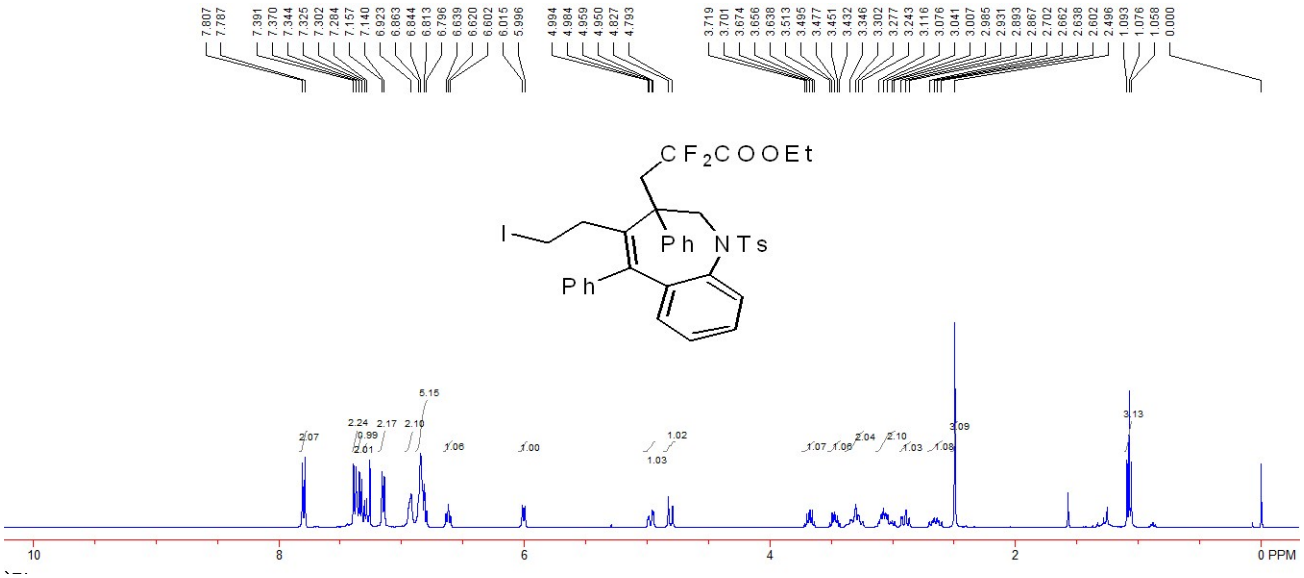
Hz, $J_2$ = 3.2 Hz), 7.09 (d, 2H, $J$ = 8.4 Hz), 7.31 (d, 2H, $J$ = 8.0 Hz), 7.69 (d, 2H, $J$ = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.6, 13.7, 21.6, 25.3, 37.6, 41.2, 43.5 (t, $J_{C\text{-}F}$ = 21.2 Hz), 55.19, 55.25, 62.9, 67.0, 113.1, 113.9, 115.7 (t, $J_{C\text{-}F}$ = 252.3 Hz), 115.8, 127.1, 128.7, 129.0, 129.7, 130.3, 134.6, 139.0, 139.8, 142.4, 143.4, 145.1, 158.6, 159.4, 164.1 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -100.3 (ddd, 1F, $J_1$ = 258.3 Hz, $J_2$ = 24.4 Hz, $J_3$ = 13.5 Hz), -102.4 (ddd, 1F, $J_1$ = 258.3 Hz, $J_2$ = 21.8 Hz, $J_3$ = 10.9 Hz); MS (ESI) *m/z*: 740.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{33}H_{37}F_2INO_6S^+$ requires: 740.1349, Found: 740.1345.

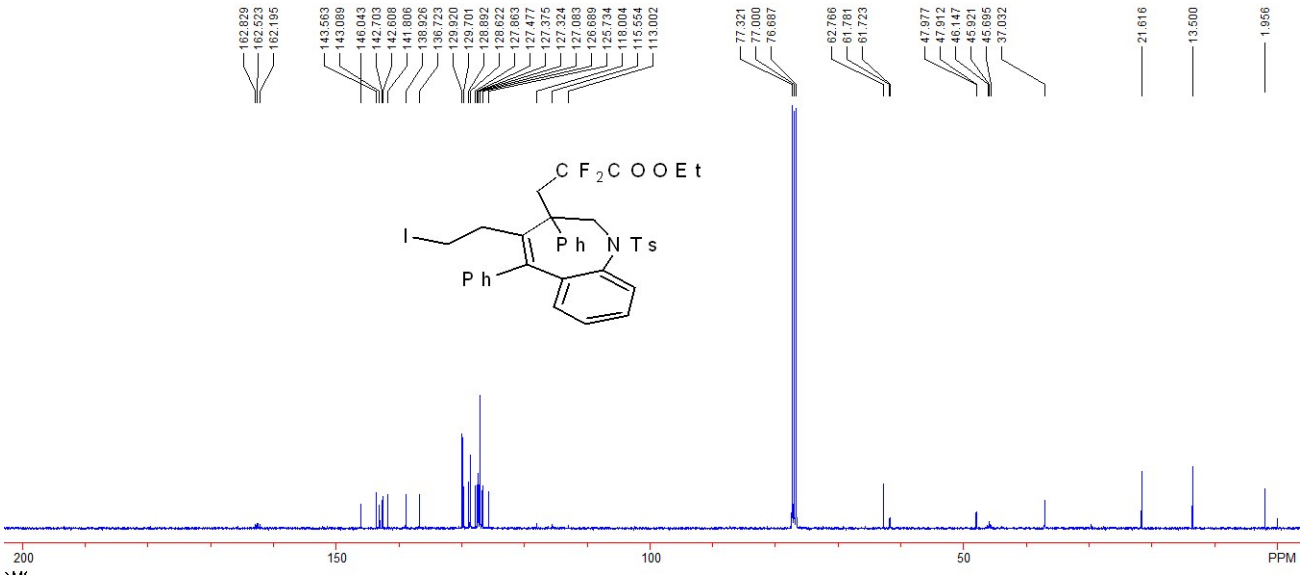


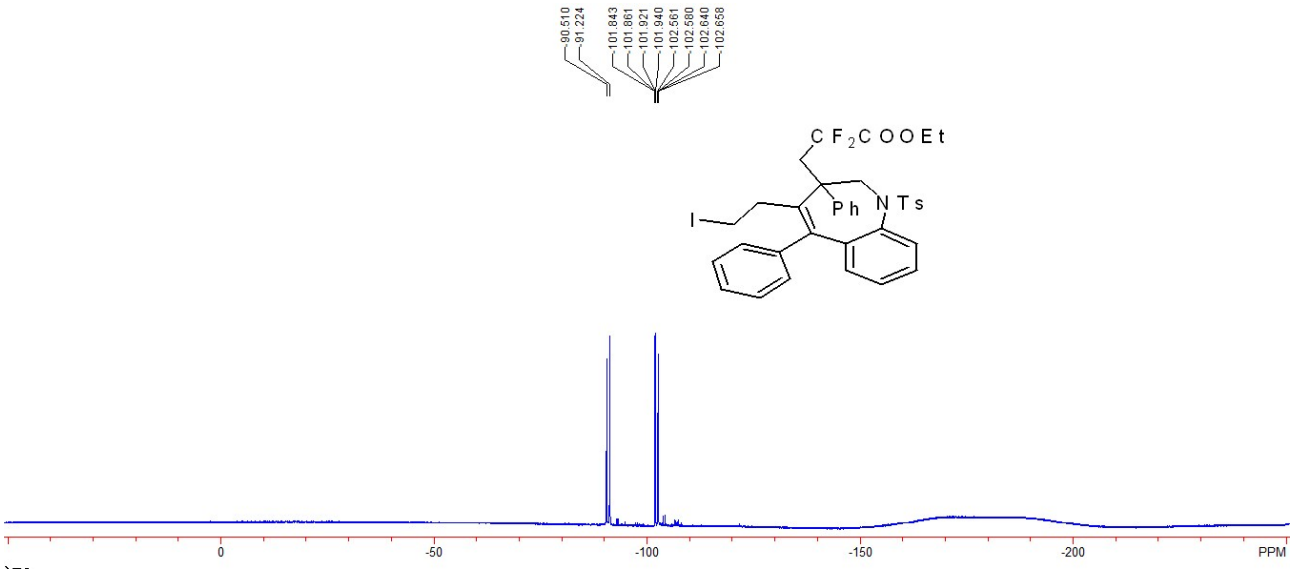


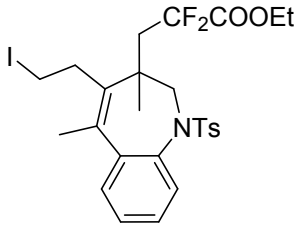




**Compound 2v**: 98 mg, 88%, A white solid, m.p. 168-170 $^{o}$C; IR ($CH_2Cl_2$): ν 3060, 2963, 2923, 2853, 1764, 1649, 1494, 1340, 1304, 1162, 1092, 1079, 1061, 766, 703, 661 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.08 (t, 3H, $J$ = 7.2 Hz), 2.50 (s, 3H), 2.60-2.70 (m, 1H), 2.87-2.93 (m, 1H), 2.99-3.12 (m, 2H), 3.24-3.35 (m, 2H), 3.43-3.51 (m, 1H), 3.64-3.72 (m, 1H), 4.81 (d, 1H, $J$ = 13.6 Hz), 4.97 (dd, 1H, $J_1$ = 13.6 Hz, $J_2$ = 3.6 Hz), 6.01 (d, 1H, $J$ = 7.6 Hz), 6.62 (t, 1H, $J$ = 7.6 Hz), 6.80-6.86 (m, 5H), 6.92 (brs, 2H), 7.15 (d, 2H, $J$ = 6.8 Hz), 7.29 (d, 1H, $J$ = 6.8 Hz), 7.33 (d, 2H, $J$ = 7.6 Hz), 7.38 (d, 2H, $J$ = 8.0 Hz), 7.80 (d, 2H, $J$ = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.0, 13.5, 21.6, 37.0, 45.9 (t, $J_{C\text{-}F}$ = 22.6 Hz), 47.9 (t, $J_{C\text{-}F}$ = 6.5 Hz), 61.8 (t, $J_{C\text{-}F}$ = 5.8 Hz), 62.8, 115.6 (t, $J_{C\text{-}F}$ = 255.2 Hz), 125.7, 126.7, 127.1, 127.3, 127.4, 127.5, 127.9, 128.6, 128.9, 129.7, 129.9, 136.7, 138.9, 141.8, 142.6, 142.7, 143.1, 143.6, 146.0 162.5 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -90.9 (d, 1F, $J$ = 268.5 Hz), -102.3 (ddd, 1F, $J_1$ = 268.5 Hz, $J_2$ = 29.3 Hz, $J_3$ = 6.8 Hz); MS (ESI) *m/z*: 759.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{36}H_{38}F_2IN_2O_4S^+$ requires: 759.1560, Found: 759.1557.

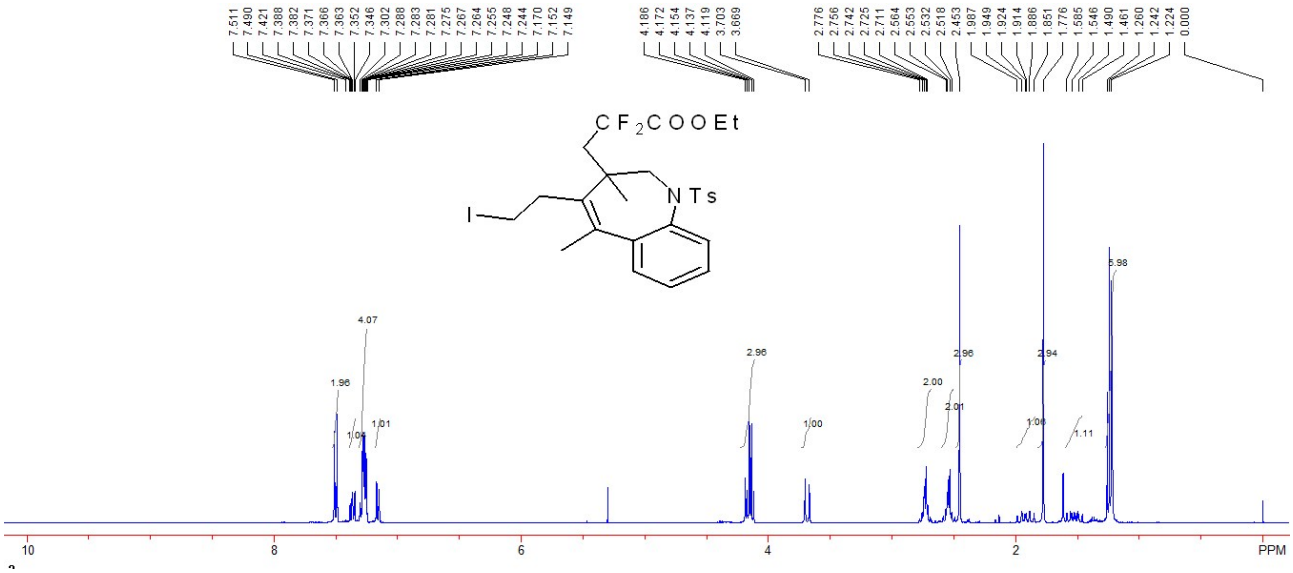

7.807
7.787
7.391
7.370
7.344
7.325
7.302
7.284
7.157
7.140
6.923
6.863
6.844
6.813
6.796
6.639
6.620
6.602
6.015
5.996
4.994
4.984
4.959
4.950
4.827
4.793
3.719
3.701
3.674
3.656
3.638
3.513
3.495
3.477
3.451
3.432
3.346
3.302
3.277
3.243
3.116
3.076
3.041
3.007
2.985
2.931
2.893
2.867
2.702
2.662
2.638
2.602
2.496
1.093
1.076
1.058
0.000
CF2COOEt
I
Ph
NTs
Ph
2.07
2.24
0.99
2.01
2.17
5.15
2.10
1.06
1.00
1.02
1.03
1.07
1.05
2.04
2.10
1.03
1.08
3.09
3.13
10
8
6
4
2
0 PPM

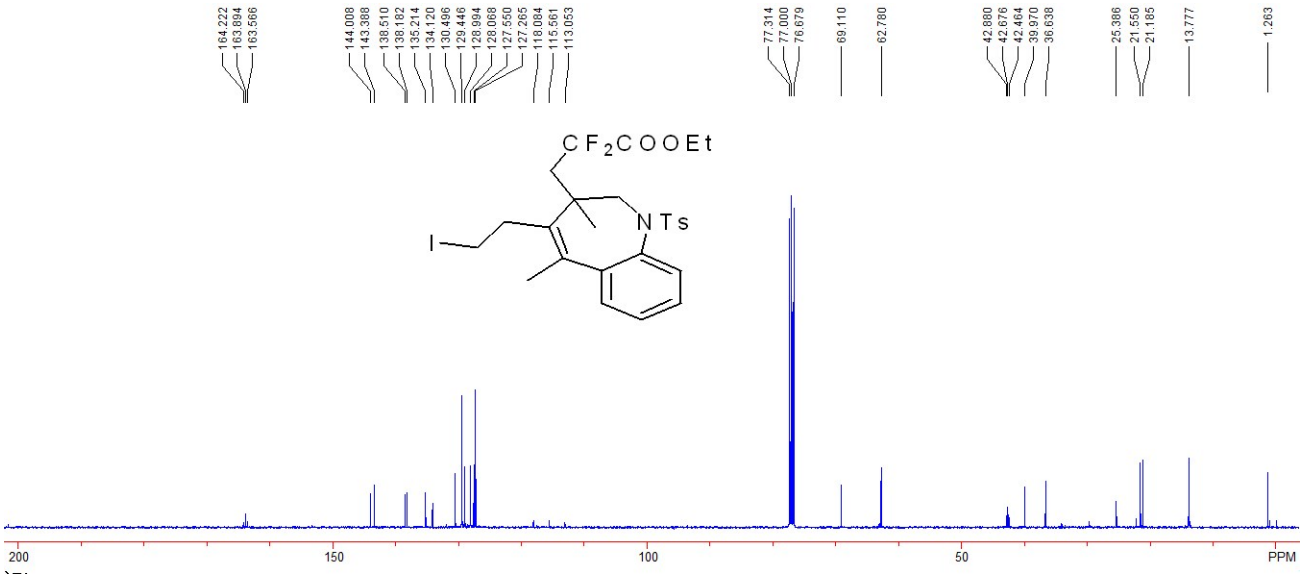

162.829
162.523
162.195
143.563
143.089
146.043
142.703
142.608
141.806
138.926
136.723
129.920
129.701
128.892
128.622
127.863
127.477
127.375
127.324
127.083
126.689
125.734
119.004
115.534
113.002
77.321
77.000
76.687
62.766
61.781
61.723
47.977
47.912
46.147
45.921
45.695
37.032
21.616
13.500
1.956
CF2COOEt
I
Ph
NTs
Ph
200
150
100
50
PPM

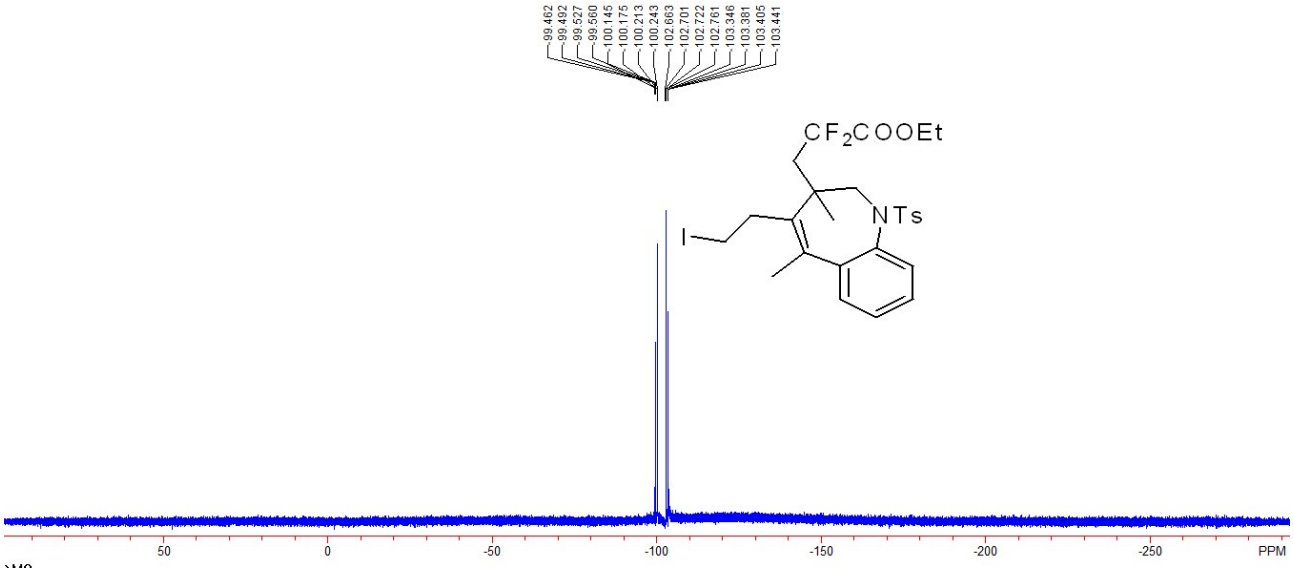

90.510
91.224
101.843
101.861
101.921
101.940
102.561
102.580
102.640
102.658
CF2COOEt
I
Ph
NTs
0
-50
-100
-150
-200
PPM



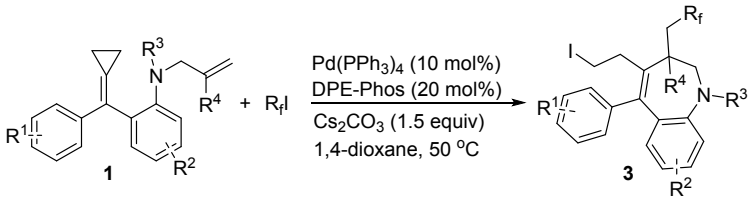

**Compound 2x**: 74 mg, 80%, A white solid, m.p. 99-101 $^{o}$C; IR ($CH_2Cl_2$): ν 3057, 2985, 2956, 2862, 1768, 1489, 1341, 1166, 1091, 1034, 865, 705 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.22 (s, 3H), 1.24 (t, 3H, $J$ = 7.2 Hz), 1.46-1.59 (m, 1H), 1.78 (s, 3H), 1.85-1.99 (m, 1H), 2.45 (s, 3H), 2.52-2.56 (m, 2H), 2.71-2.78 (m, 2H), 3.68 (d, 1H, $J$ = 13.6 Hz), 4.12-4.19 (m, 3H), 7.16 (dd, 1H, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz), 7.24-7.30 (m, 4H), 7.35-7.39 (m, 1H), 7.50 (d, 2H, $J$ = 8.4 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 1.3, 13.8, 21.2, 21.6, 25.4, 36.6, 40.0, 42.7 (t, $J_{C\text{-}F}$ = 21.2 Hz), 62.8, 69.1, 115.6 (t, $J_{C\text{-}F}$ = 252.3 Hz), 127.3, 127.6, 128.1, 129.0, 129.4, 130.5, 134.1, 135.2, 138.2, 138.5, 143.4, 144.0, 163.9 (t, $J_{C\text{-}F}$ = 32.8 Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -99.8 (ddd, 1F, $J_1$ = 256.8 Hz, $J_2$ = 24.4 Hz, $J_3$ = 11.3 Hz), -103.0 (ddd, 1F, $J_1$ = 256.8 Hz, $J_2$ = 22.2 Hz, $J_3$ = 13.5 Hz); MS (ESI) *m/z*: 635.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{34}F_2IN_2O_4S^+$ requires: 635.1247, Found: 635.1248.




164.222
163.894
163.566
144.008
143.388
138.510
138.182
135.214
134.120
130.496
129.446
128.994
128.068
127.550
127.265
118.084
115.561
113.053
77.314
77.000
76.679
69.110
62.780
42.880
42.676
42.464
39.970
36.638
25.386
21.550
21.185
13.777
1.263
CF2COOEt
NTs
I
200
150
100
50
PPM

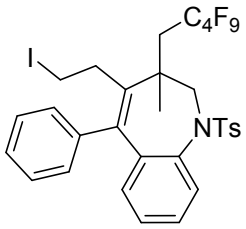

99.462
99.492
99.527
99.560
100.145
100.175
100.213
100.243
102.663
102.701
102.722
102.761
103.346
103.381
103.405
103.441
CF2COOEt
NTs
I
50
0
-50
-100
-150
-200
-250
PPM

**General procedure for the synthesis of products 3**

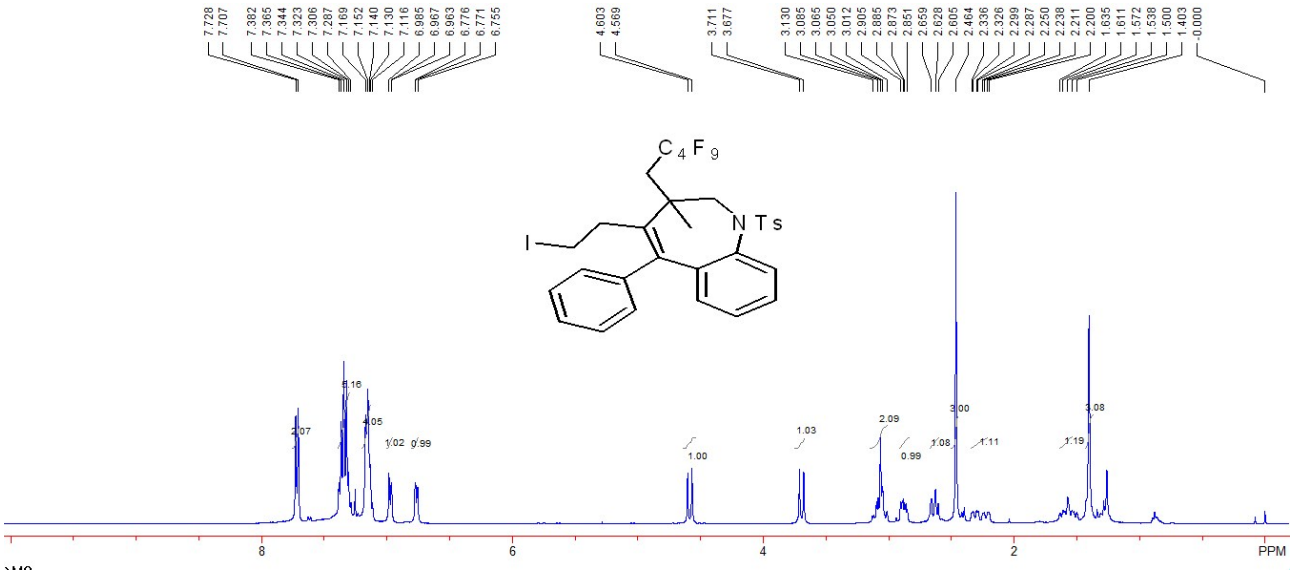


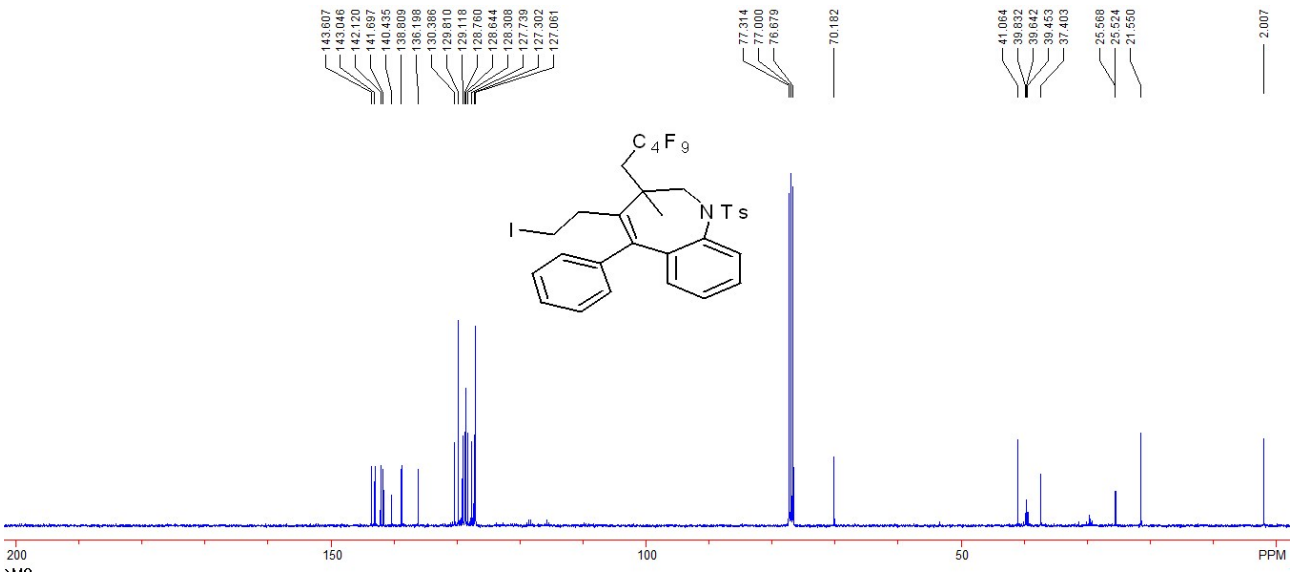

**1** (0.15 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (0.015 mmol, 0.10 equiv), DPE-Phos (0.030 mmol, 0.20 equiv) and $Cs_2CO_3$ (0.225 mmol, 1.5 equiv) were dissolved in super-dry 1,4-dioxane (1.5 mL), then perfluoroalkyl reagent $R_fI$ (0.30 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 50 $^oC$ oil bath. The reaction was stopped after 5 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 15 / 1) to afford the products **3** in good yields.

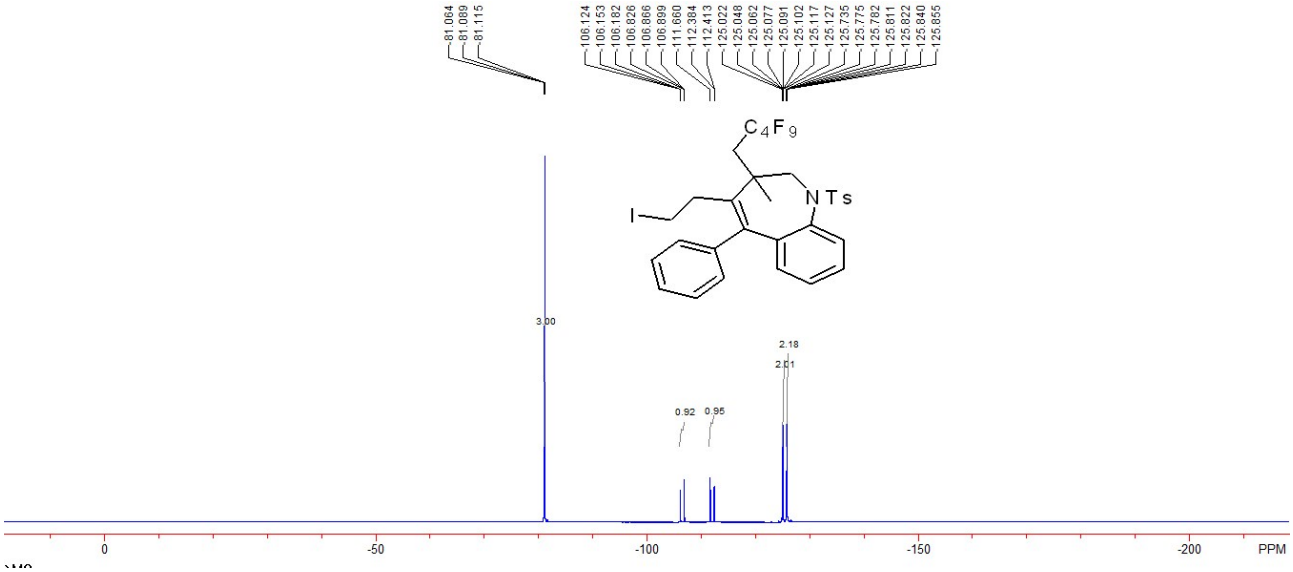
**Spectroscopic data for products 3**

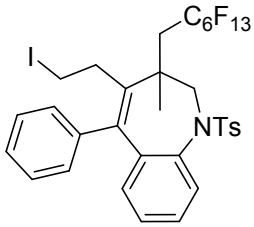



**Compound 3aa**: 84 mg, 72%, A white solid, m.p. 133-135 °C; IR ($CH_2Cl_2$): ν 3059, 2974, 2923, 2893, 1597, 1487, 1344, 1234, 1219, 1155, 1134, 1092, 1047, 1023, 881, 730, 705, 660 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.40 (s, 3H), 1.50-1.64 (m, 1H), 2.20-2.34 (m, 1H), 2.46 (s, 3H), 2.61-2.66 (m, 1H), 2.85-2.91 (m, 1H), 3.01-3.13 (m, 2H), 3.69 (d, 1H, $J$ = 13.6 Hz), 4.59 (d, 1H, $J$ = 13.6 Hz), 6.77 (dd, 1H, $J_1$ = 8.4 Hz, $J_2$ = 1.6 Hz), 6.97 (dd, 1H, $J_1$ = 8.4 Hz, $J_2$ = 1.6 Hz), 7.12-7.17 (m, 4H), 7.29-7.38 (m, 5H), 7.72 (d, 2H, $J$ = 8.4 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 2.0, 21.6, 25.6 (t, $J_{C\text{-}F}$ = 4.4 Hz), 37.4, 39.6 (t, $J_{C\text{-}F}$ = 19.0 Hz), 41.1, 70.2, 100-120 (m), 127.1, 127.3, 127.7, 128.3, 128.6, 128.8, 129.1, 129.8, 130.4, 136.2, 138.8, 140.4 (t, $J_{C\text{-}F}$ = 1.4 Hz), 141.7, 142.1, 143.0, 143.6; $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -81.1 (t, 3F, $J$ = 9.8 Hz), -106.1 - -106.9 (m, 1F), -111.7 - -112.4 (m, 1F), -125.0 - -125.1 (m, 2F), -125.7 - -125.9 (m, 2F); MS (ESI) *m/z*: 793.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{31}F_9IN_2O_2S^+$ requires: 793.1002, Found: 793.1002.



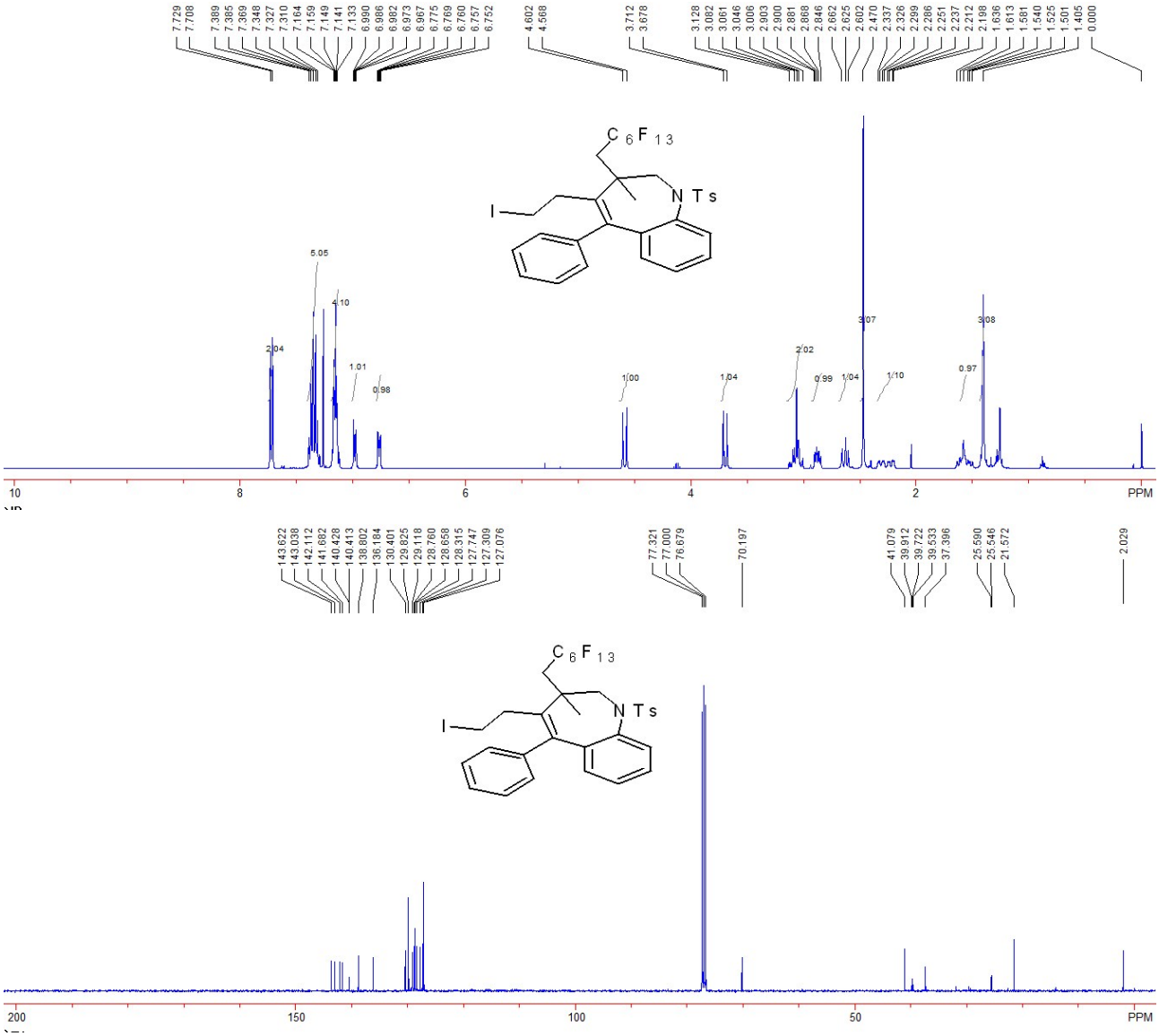


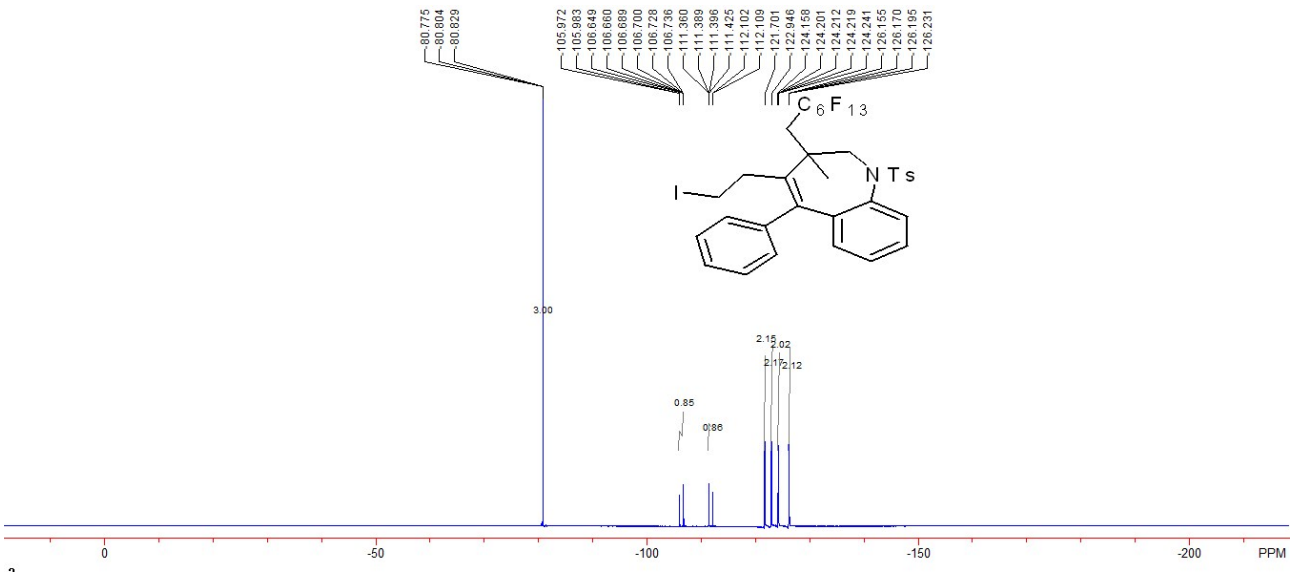



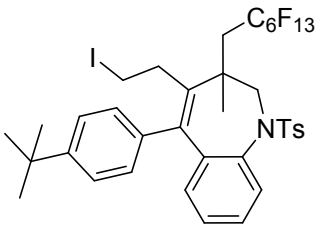




**Compound 3ab**: 102 mg, 78%, A white solid, m.p. 143-145 $^{o}$C; IR ($CH_2Cl_2$): ν 2973, 2928, 2886, 1489, 1380, 1240, 1158, 1134, 1088, 1046, 880, 812, 738, 706 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.41 (s, 3H), 1.50-1.64 (m, 1H), 2.27 (qd, 1H, $J_1$ = 15.6 Hz, $J_2$ = 5.6 Hz), 2.47 (s, 3H), 2.60-2.66 (m, 1H), 2.86-2.90 (m, 1H), 3.01-3.13 (m, 2H), 3.70 (d, 1H, $J$ = 13.6 Hz), 4.59 (d, 1H, $J$ = 13.6 Hz), 6.75-6.78 (m, 1H), 6.97-6.99 (m, 1H), 7.13-7.16 (m, 4H), 7.29-7.39 (m, 5H), 7.72 (d, 2H, $J$ = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.0, 21.6, 25.6 (t, $J_{C\text{-}F}$ = 4.4 Hz), 37.4, 39.7 (t, $J_{C\text{-}F}$ = 19.0 Hz), 41.1, 70.2, 100-120 (m), 127.1, 127.3, 127.7, 128.3, 128.7, 128.8, 129.1, 129.8,

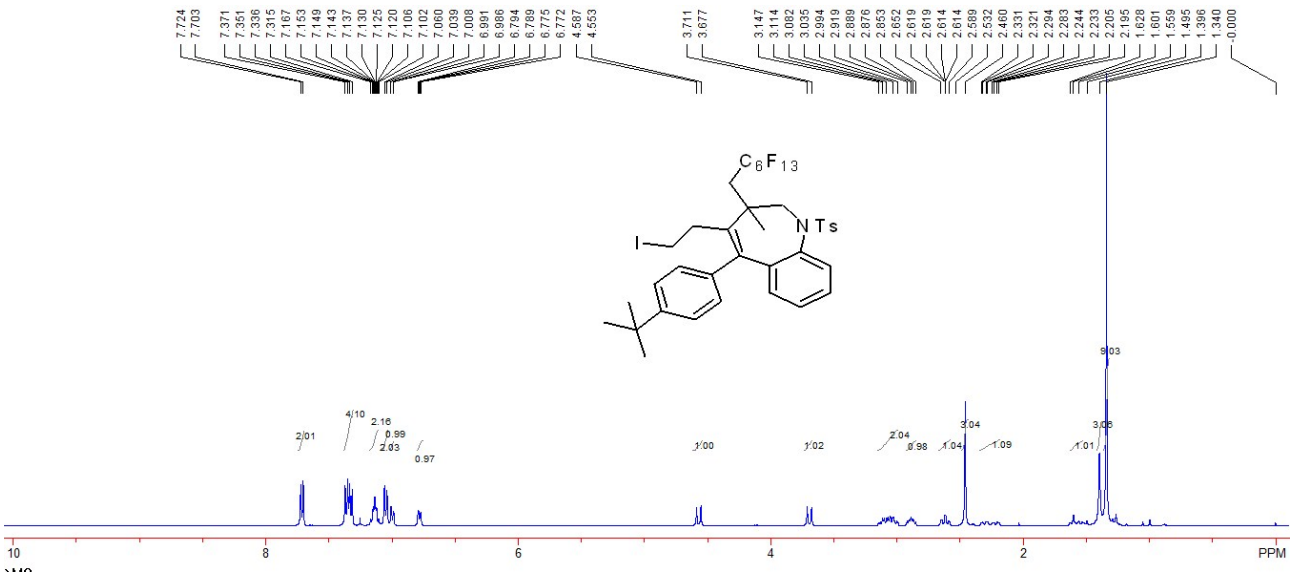
130.4, 136.2, 138.8, 140.4 (t, $J_{C\text{-}F}$ = 1.5 Hz), 141.7, 142.1, 143.0, 143.6; $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -80.8 (t, 3F, $J$ = 9.4 Hz), -106.0 - -106.7 (m, 1F), -111.4 - -112.1 (m, 1F), -121.7 (brs, 2F), -122.9 (brs, 2F), -124.16 - -124.24 (m, 2F), -126.16 - -126.23 (m, 2F); MS (ESI) *m/z*: 893.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{33}H_{31}F_{13}IN_2O_2S^+$ requires: 893.0938, Found: 893.0937.

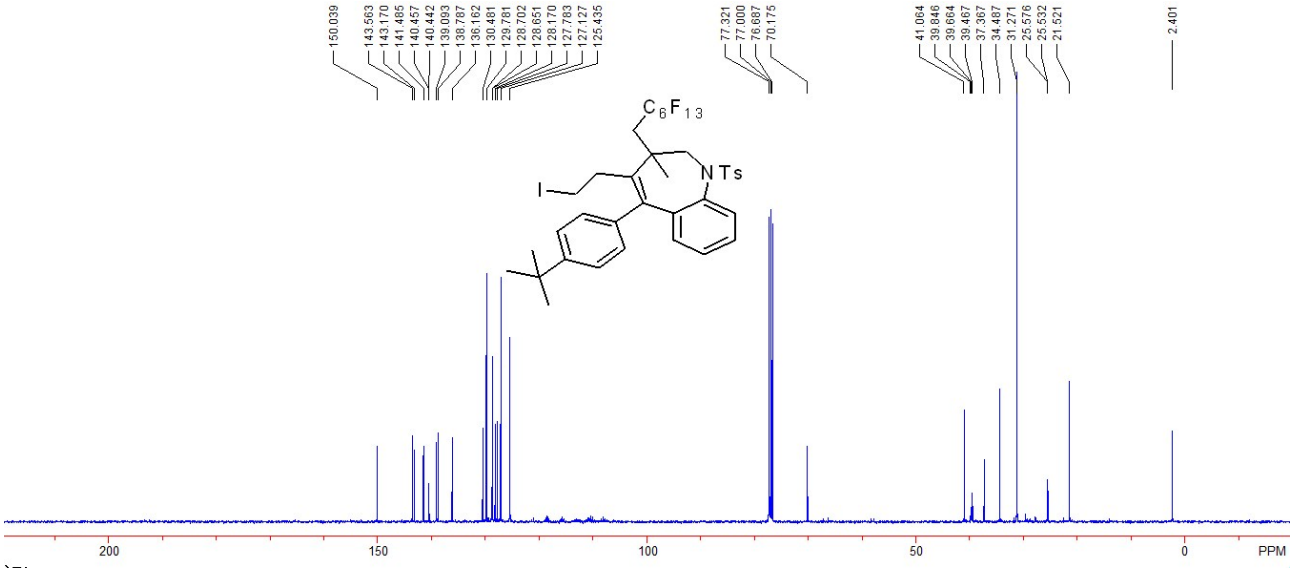


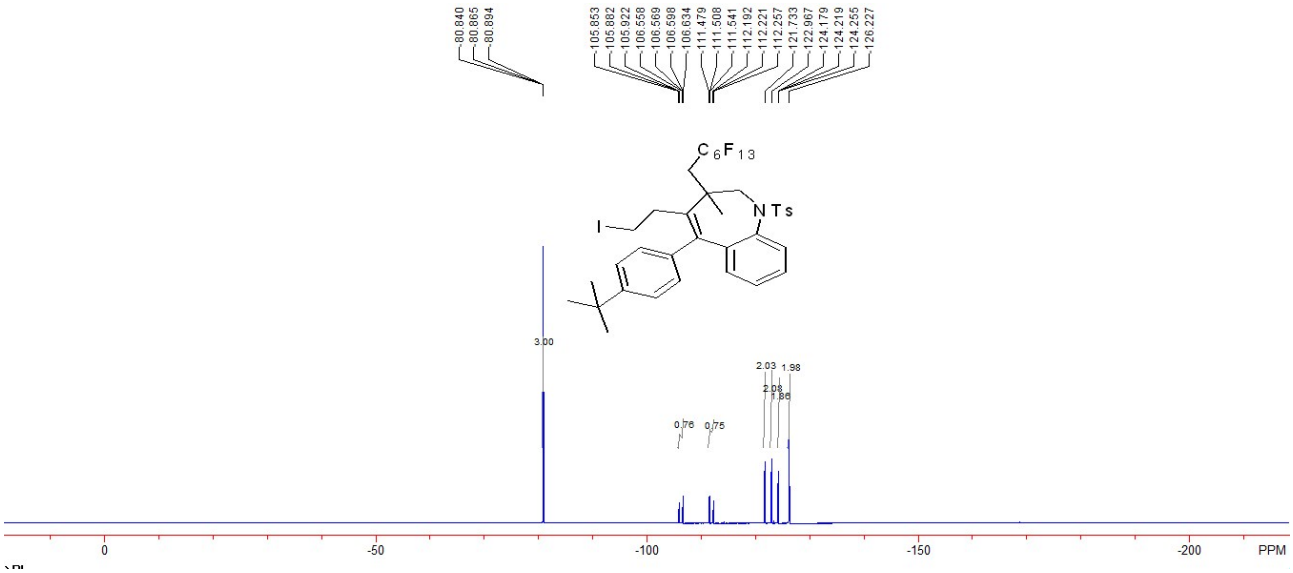


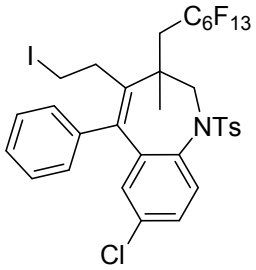




**Compound 3eb**: 117 mg, 84%, A white solid, m.p. 155-157 $^{o}$C; IR ($CH_2Cl_2$): ν 2970, 2898, 2873, 1487, 1344, 1239, 1145, 1091, 1047, 880, 812, 769, 732, 657 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.34 (s, 9H), 1.40 (s, 3H), 1.50-1.63 (m, 1H), 2.26 (qd, 1H, $J_1$ = 15.2 Hz, $J_2$ = 4.0 Hz), 2.46 (s, 3H), 2.59-2.65 (m, 1H), 2.85-2.92 (m, 1H), 2.99-3.15 (m, 2H), 3.69 (d, 1H, $J$ = 13.6 Hz), 4.57 (d, 1H, $J$ = 13.6 Hz), 6.78 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz), 7.00 (dd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz), 7.05 (d, 2H, $J$ = 8.4 Hz), 7.10-7.17 (m, 2H), 7.32-7.37 (m, 4H), 7.71 (d, 2H, $J$ = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.4, 21.5, 25.6 (t, $J_{C\text{-}F}$ = 4.4 Hz), 31.3, 34.5, 37.4, 39.7 (t, $J_{C\text{-}F}$ = 19.0 Hz), 41.1, 70.2, 100-120 (m), 125.4, 127.1, 127.8, 128.2, 128.65, 128.70, 129.8, 130.5, 136.2, 138.8, 139.1, 140.4 (t, $J_{C\text{-}F}$ = 1.5 Hz), 140.5, 141.5, 143.2, 143.6. 150.0; $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -80.9 (t, 3F, $J$ = 9.4 Hz), -105.9 - -106.6 (m, 1F), -111.5 - -112.3 (m, 1F), -121.7 (brs, 2F), -123.0 (brs, 2F), -124.2 - -124.3 (m, 2F), -126.2 (brs, 2F); MS (ESI) *m/z*: 949.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{37}H_{39}F_{13}IN_2O_2S^+$ requires: 949.1564, Found: 949.1565.

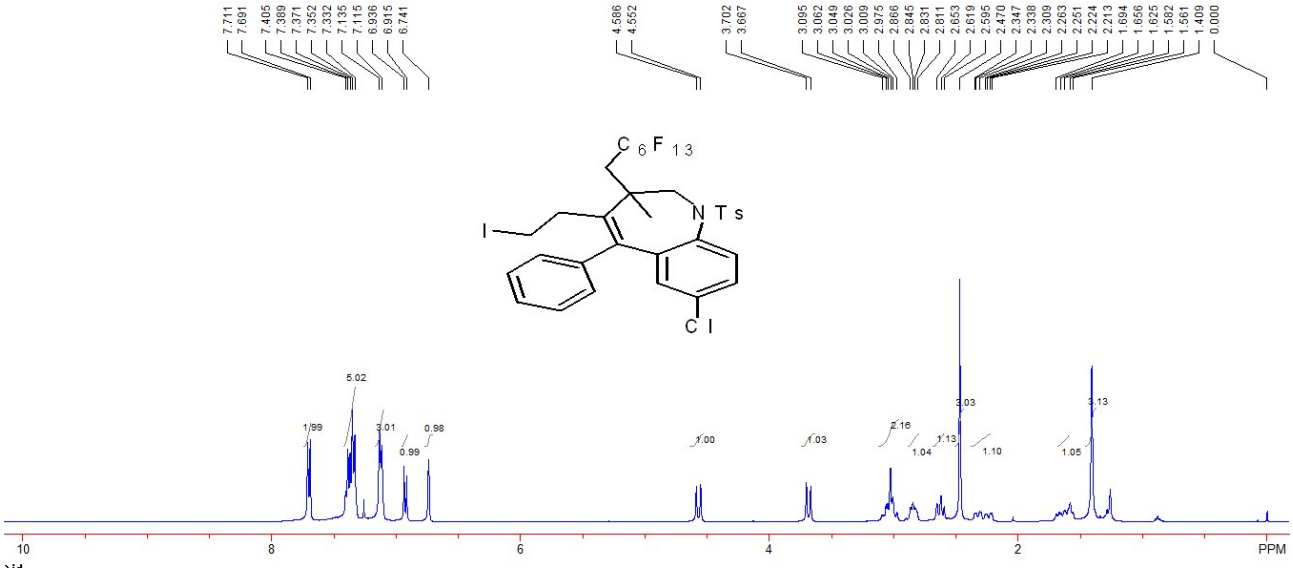

7.724
7.703
7.371
7.351
7.336
7.315
7.167
7.153
7.149
7.143
7.137
7.130
7.125
7.120
7.106
7.102
7.060
7.039
7.008
6.991
6.986
6.794
6.789
6.775
6.772
4.587
4.553
3.711
3.677
3.147
3.114
3.082
3.035
2.994
2.919
2.889
2.876
2.853
2.652
2.619
2.619
2.614
2.614
2.589
2.532
2.460
2.331
2.321
2.294
2.283
2.244
2.233
2.205
2.195
1.628
1.601
1.559
1.495
1.396
1.340
-0.000
C6F13
NTs
I
2.01
4.10
2.16
0.99
2.03
0.97
1.00
1.02
2.04
0.98
1.04
3.04
1.09
1.01
3.08
9.03
10
8
6
4
2
PPM

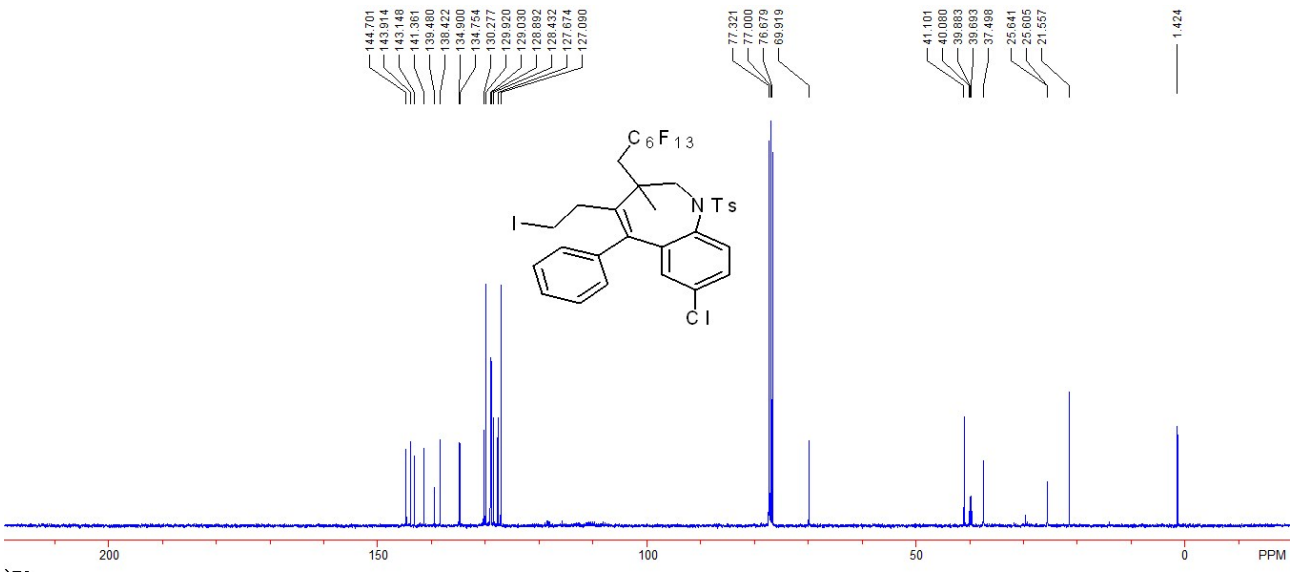

150.039
143.563
143.170
141.465
140.457
140.442
139.093
138.787
136.162
130.481
129.781
128.702
128.651
128.170
127.783
127.127
125.435
77.321
77.000
76.687
70.175
41.064
39.846
39.664
39.467
37.367
34.487
31.271
25.576
25.532
21.521
2.401
C6F13
NTs
I
200
150
100
50
0
PPM

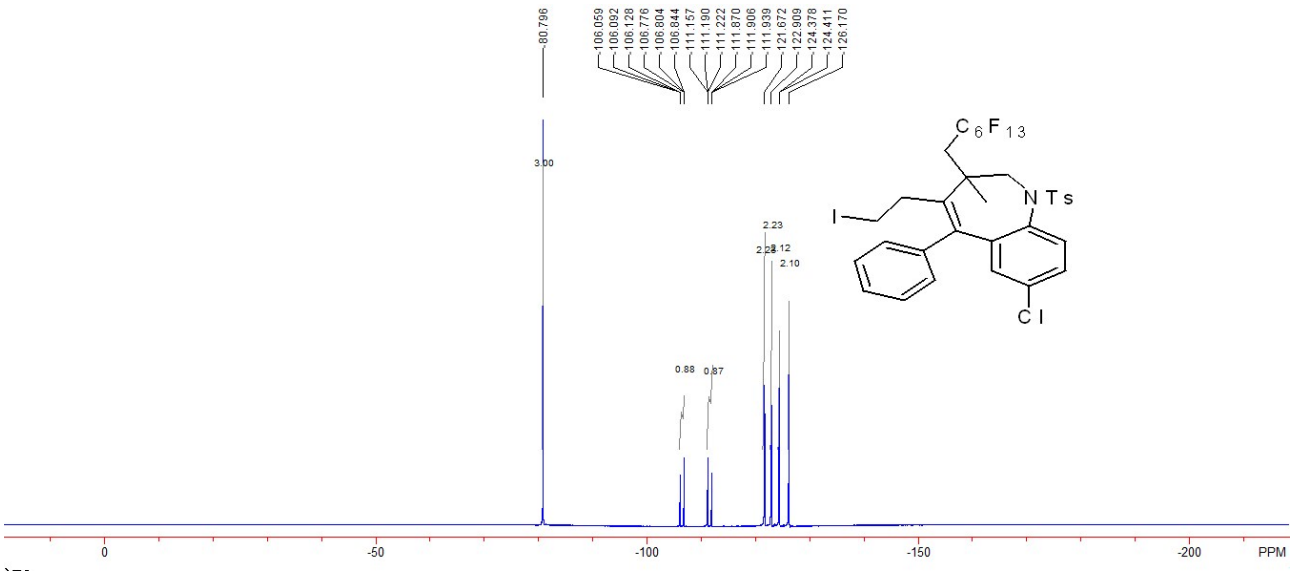

80.840
80.865
80.894
105.853
105.882
105.922
106.558
106.569
106.598
106.634
111.479
111.508
111.541
112.192
112.221
112.257
121.733
122.967
124.179
124.219
124.255
126.227
C6F13
NTs
I
3.00
2.03
1.98
2.08
1.86
0.76
0.75
0
-50
-100
-150
-200
PPM

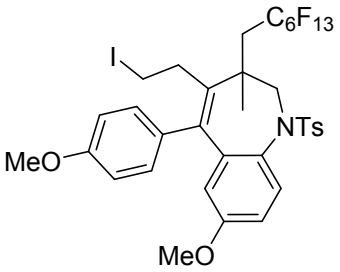



**Compound 3nb**: 97 mg, 71%, A white solid, m.p. 134-136 °C; IR ($CH_2Cl_2$): ν 2974, 2923, 2893, 1597, 1483, 1344, 1238, 1145, 1091, 1046, 880, 813, 706, 657 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.41 (s, 3H), 1.56-1.69 (m, 1H), 2.29 (qd, 1H, $J_1$ = 15.2 Hz, $J_2$ = 4.0 Hz), 2.47 (s, 3H), 2.60-2.65 (m, 1H), 2.81-2.87 (m, 1H), 2.98-3.10 (m, 2H), 3.68 (d, 1H, $J$ = 13.6 Hz), 4.57 (d, 1H, $J$ = 13.6 Hz), 6.74 (s, 1H), 6.93 (d, 1H, $J$ = 7.6 Hz), 7.34 (d, 3H, $J$ = 8.0 Hz), 7.37-7.41 (m, 5H), 7.70 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 1.4, 21.6, 25.6 (t, $J_{C-F}$ = 3.6 Hz), 37.5, 39.9 (t, $J_{C-F}$ = 19.0 Hz), 41.1, 69.9, 100-120 (m), 127.1, 127.7, 128.4, 128.9, 129.0, 129.9, 130.3, 134.8, 134.9, 138.4, 139.5 (t, $J_{C-F}$ = 2.2 Hz), 141.4, 143.1, 143.9, 144.7; $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -80.8 (brs, 3F), -106.1 - -106.8 (m, 1F), -111.2 - -111.9 (m, 1F), -121.7 (brs, 2F), -122.9 (brs, 2F), -124.38 - -124.41 (m, 2F), -126.2 (brs, 2F); MS (ESI) *m/z*: 927.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{33}H_{30}ClF_{13}IN_2O_2S^+$ requires: 927.0548, Found: 927.0546.



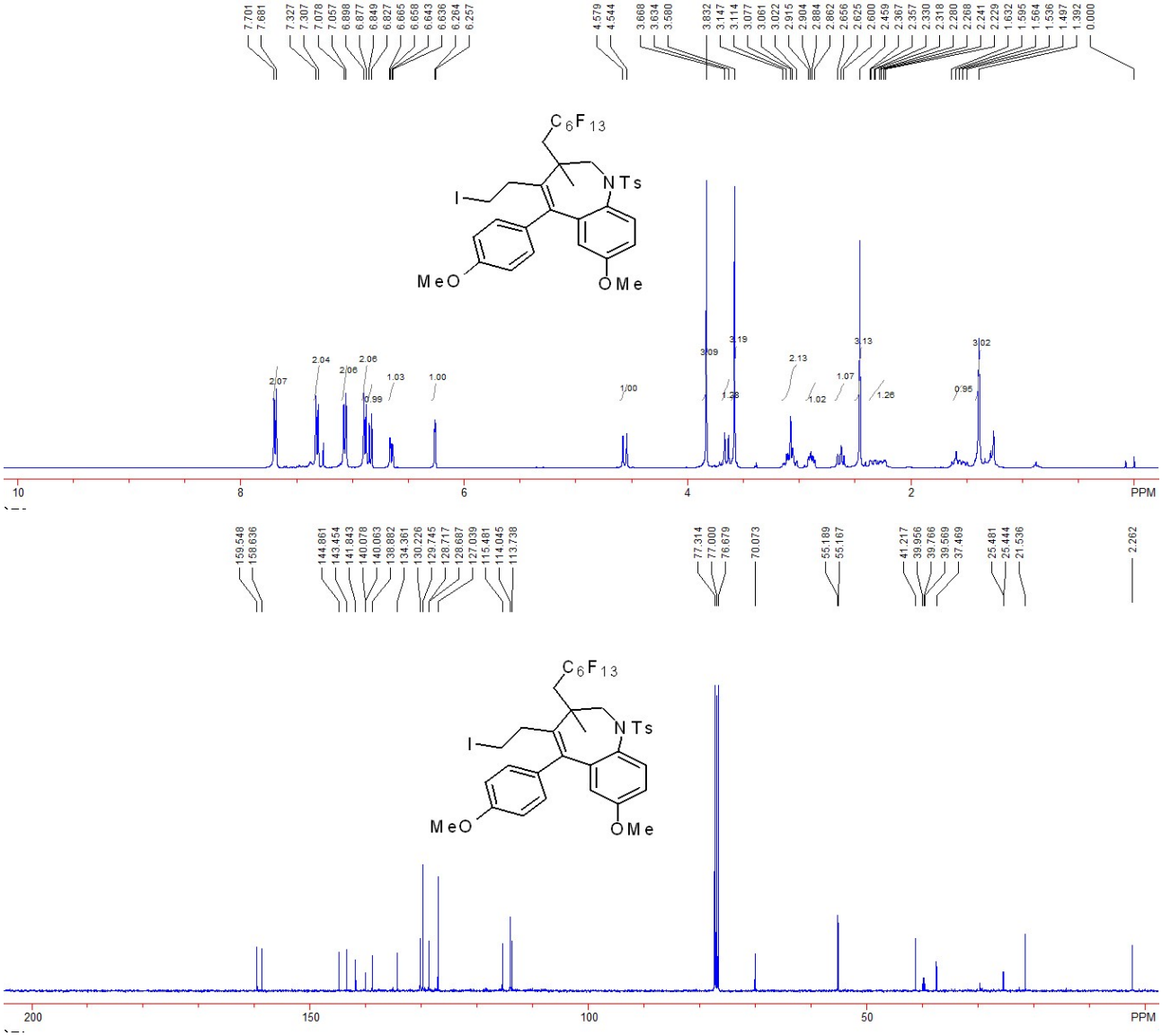


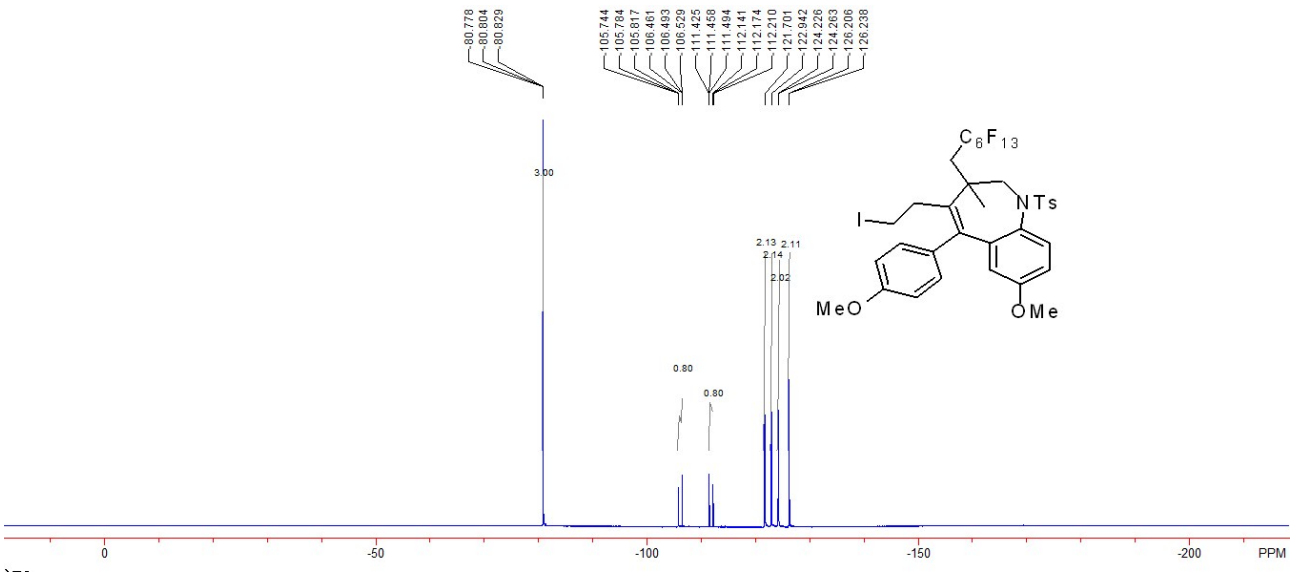



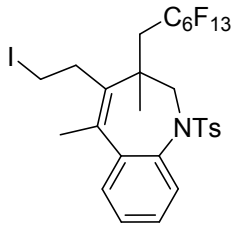




**Compound 3rb**: 114 mg, 81%, A white solid, m.p. 144-146 $^{o}$C; IR ($CH_2Cl_2$): ν 2973, 2925, 2886, 1505, 1451, 1380, 1327, 1241, 1089, 1046, 880, 816, 715, 660 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.39 (s, 3H), 1.50-1.63 (m, 1H), 2.23-2.41 (m, 1H), 2.46 (s, 3H), 2.60-2.66 (m, 1H), 2.86-2.92 (m, 1H), 3.02-3.15 (m, 2H), 3.58 (s, 3H), 3.65 (d, 1H, $J$ = 13.6 Hz), 3.83 (s, 3H), 4.56 (d, 1H, $J$ = 13.6 Hz), 6.26 (d, 1H, $J$ = 2.8 Hz), 6.65 (dd, 1H, $J_1$ = 8.8 Hz, $J_2$ = 2.8 Hz), 6.84 (d, 1H, $J$ = 8.8 Hz), 6.89 (d, 2H, $J$ = 8.4 Hz), 7.07 (d, 2H, $J$ = 8.4 Hz), 7.32 (d, 2H, $J$ = 8.0 Hz), 7.69 (d, 2H, $J$ = 8.0

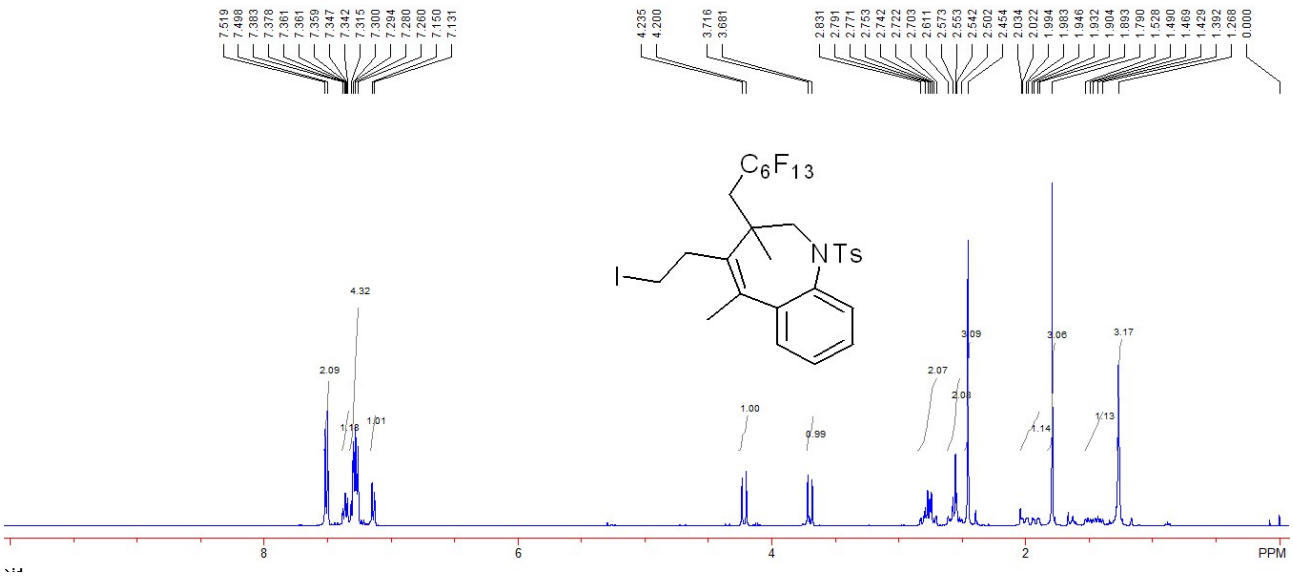
Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 2.3, 21.5, 25.5 (t, $J_{C\text{-}F}$ = 3.7 Hz), 37.5, 39.8 (t, $J_{C\text{-}F}$ = 19.0 Hz), 41.2, 55.17, 55.19, 70.1, 100-120 (m), 113.7, 114.0, 115.5, 127.0, 128.69, 128.72, 129.7, 130.2, 134.4, 138.9, 140.1 (t, $J_{C\text{-}F}$ = 1.5 Hz), 141.8, 143.5, 144.9, 158.6, 159.5; $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -80.8 (t, 3F, $J$ = 9.4 Hz), -105.7 - -106.5 (m, 1F), -111.4 - -112.2 (m, 1F), -121.7 (brs, 2F), -122.9 (brs, 2F), -124.2 - -124.3 (m, 2F), -126.21 - -126.24 (m, 2F); MS (ESI) *m/z*: 936.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{35}H_{32}F_{13}INO_4S^+$ requires: 936.0884, Found: 936.0882.

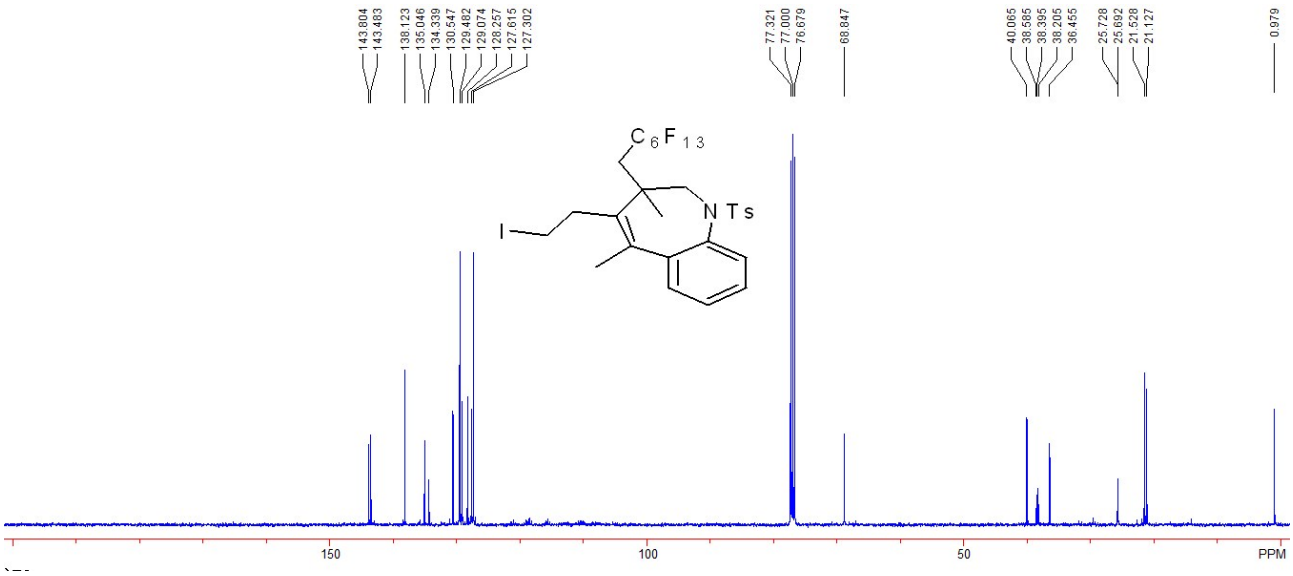


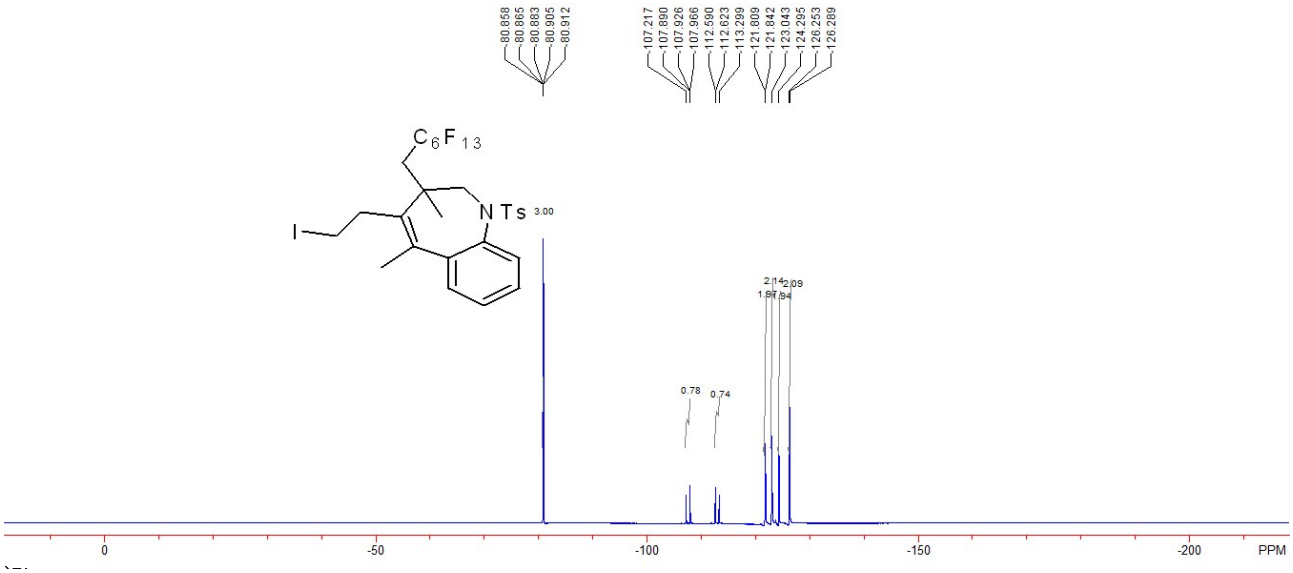


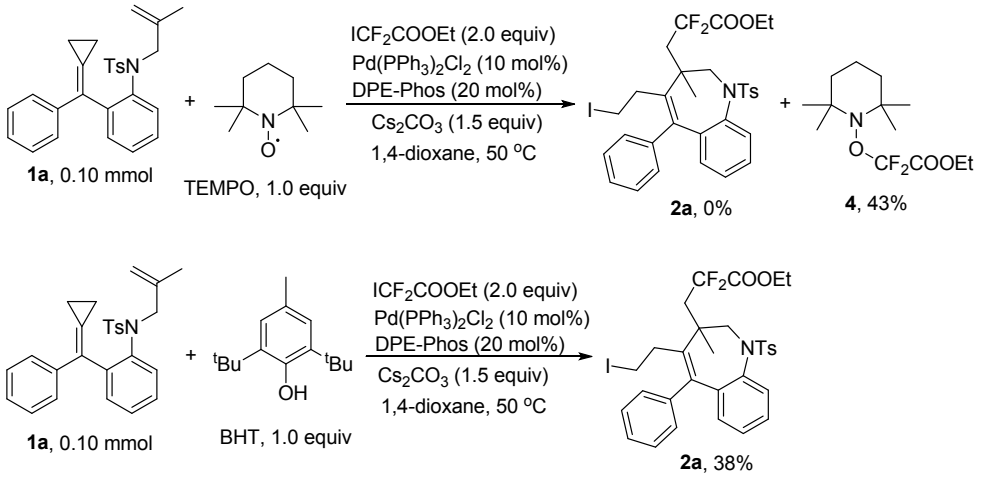

**Compound 3ub**: 98 mg, 80%, A white solid, m.p. 102-104 $^{o}$C; IR ($CH_2Cl_2$): ν 2974, 2925, 2889, 1491, 1348, 1239, 1194, 1158, 1143, 1091, 1046, 880, 813, 765, 707 $cm^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27 (s, 3H), 1.39-1.53 (m, 1H), 1.79 (s, 3H), 1.96 (qd, 1H, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz), 2.45 (s, 3H), 2.50-2.61 (m, 2H), 2.70-2.83 (m, 2H), 3.70 (d, 1H, $J$ = 13.6 Hz), 4.22 (d, 1H, $J$ = 13.6 Hz), 7.14 (d, 1H, $J$ = 7.6 Hz), 7.26-7.32 (m, 4H), 7.34-7.38 (m, 1H), 7.51 (d, 2H, $J$ = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 0.98, 21.1, 21.5, 25.7 (t, $J_{C-F}$ = 3.6 Hz), 36.5, 38.4 (t, $J_{C-F}$ = 19.0 Hz), 40.1, 68.8, 100-120 (m), 127.3, 127.6, 128.3, 129.1, 129.5, 130.5, 134.3 (t, $J_{C-F}$ = 1.5 Hz), 135.0, 138.1, 143.5, 143.8; $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -80.86 - -80.91 (m, 3F), -107.2 - -108.0 (m, 1F), -112.6 - -113.3 (m, 1F), -121.81 - -121.84 (m, 2F), -123.0 (brs, 2F), -124.3 (brs, 2F), -126.25 - -126.29 (m, 2F); MS (ESI) *m/z*: 814.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{26}F_{13}INO_2S^+$ requires: 814.0516, Found: 814.0515.


7.519
7.498
7.383
7.378
7.361
7.361
7.359
7.347
7.342
7.315
7.300
7.294
7.280
7.260
7.150
7.131
4.235
4.200
3.716
3.681
2.831
2.791
2.771
2.753
2.742
2.722
2.703
2.611
2.573
2.553
2.542
2.502
2.454
2.034
2.022
1.994
1.983
1.946
1.932
1.904
1.893
1.790
1.528
1.490
1.469
1.429
1.392
1.268
0.000
C6F13
NTs
I
4.32
2.09
1.18
1.01
1.00
0.99
2.07
2.08
3.09
3.06
1.14
1.13
3.17
8
6
4
2
PPM


143.804
143.483
138.123
135.046
134.339
130.547
129.492
129.074
128.257
127.615
127.302
77.321
77.000
76.679
68.847
40.065
38.585
38.395
38.205
36.455
25.728
25.692
21.528
21.127
0.979
C6F13
NTs
I
150
100
50
PPM


80.858
80.865
80.883
80.905
80.912
107.217
107.890
107.926
107.966
112.590
112.623
113.299
121.809
121.842
123.043
124.295
126.253
126.289
C6F13
NTs
3.00
I
2.14
2.09
1.97
1.94
0.78
0.74
0
-50
-100
-150
-200
PPM

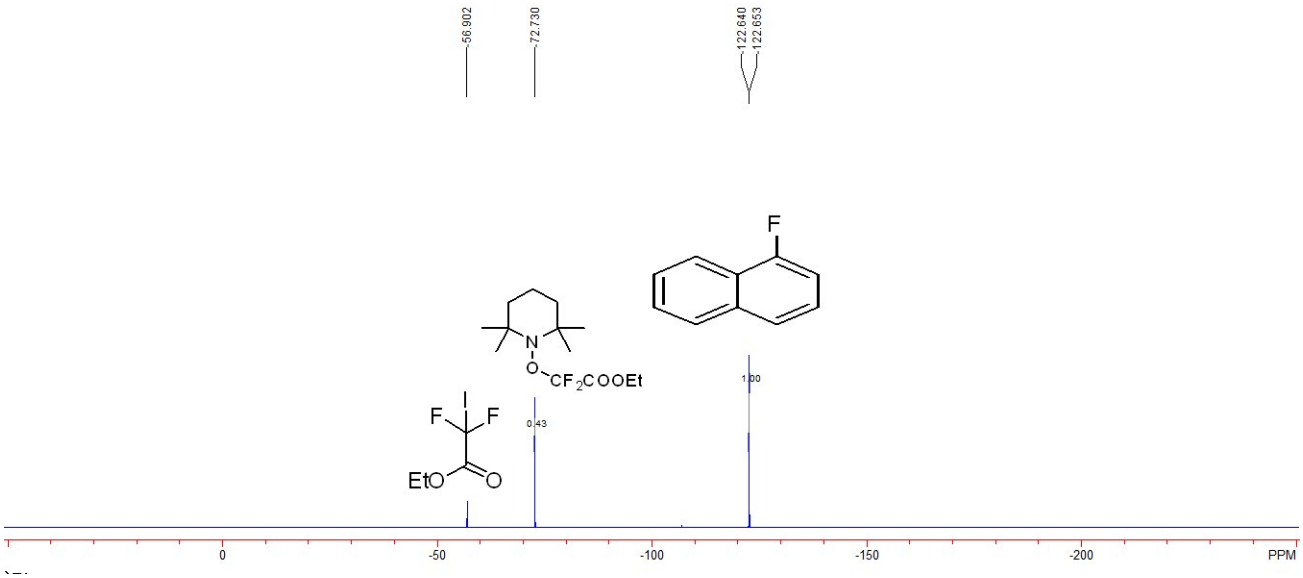
## Control experiments

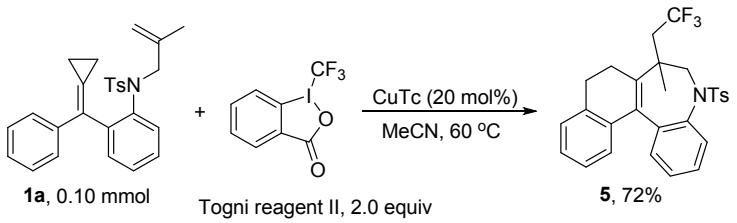



***Scheme S1*** Radical inhibition experiments

TEMPO experiment: **1a** (0.15 mmol, 1.0 equiv), TEMPO (0.15 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.015 mmol, 0.10 equiv), DPE-Phos (0.030 mmol, 0.20 equiv) and $Cs_2CO_3$ (0.225 mmol, 1.5 equiv) were dissolved in super-dry 1,4-dioxane (1.5 mL), then $ICF_2CO_2Et$ (0.30 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 50 °C oil bath. The reaction was stopped after 12 h and the reaction mixture was filtered through a celite. 1-fluoronaphthalene (77 uL) was used as an internal standard and the expected product **2a** was not detected and the TEMPO-trapped complex **4** was formed instead, which indicated a radical mechanism of this cascade reaction.

BHT experiment: **1a** (0.15 mmol, 1.0 equiv), BHT (0.15 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.015 mmol, 0.10 equiv), DPE-Phos (0.030 mmol, 0.20 equiv) and $Cs_2CO_3$ (0.225 mmol, 1.5 equiv) were dissolved in super-dry 1,4-dioxane (1.5 mL), then $ICF_2CO_2Et$ (0.30 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 50 °C oil bath. The reaction was stopped after 12 h and the reaction mixture was filtered through a celite. The expected product **2a** was isolated only in 38% yield. The reaction was suppressed to a great extent which also indicated a probable radical mechanism.

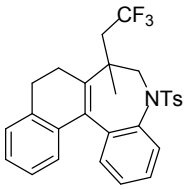


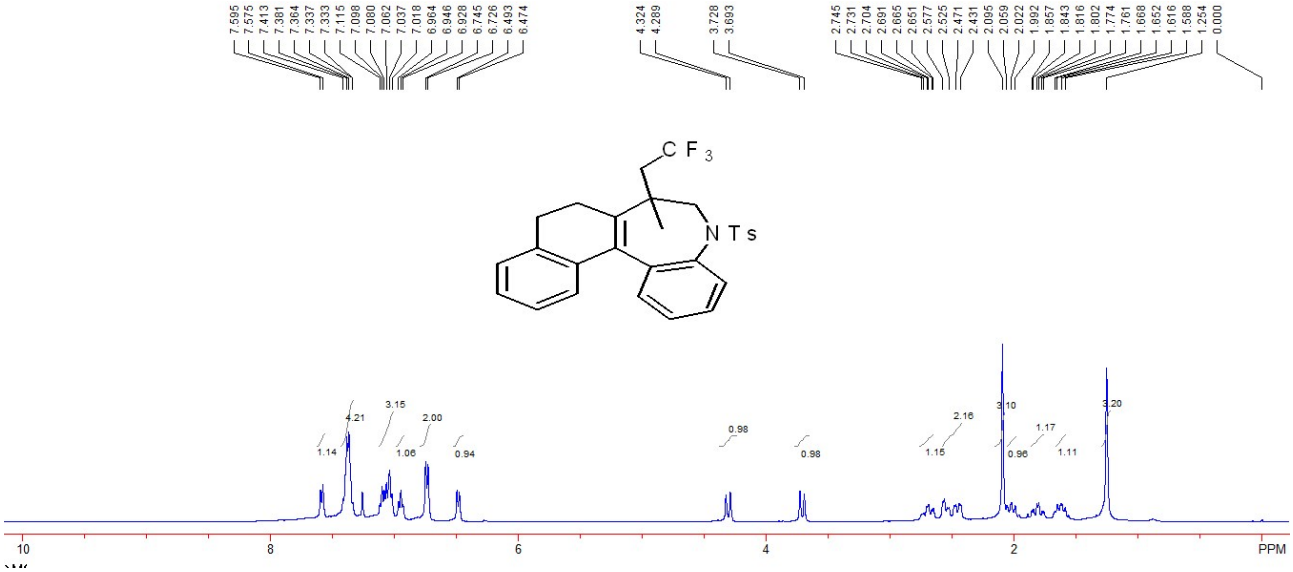

***Scheme S2*** Trifluoromethylation of **1a**

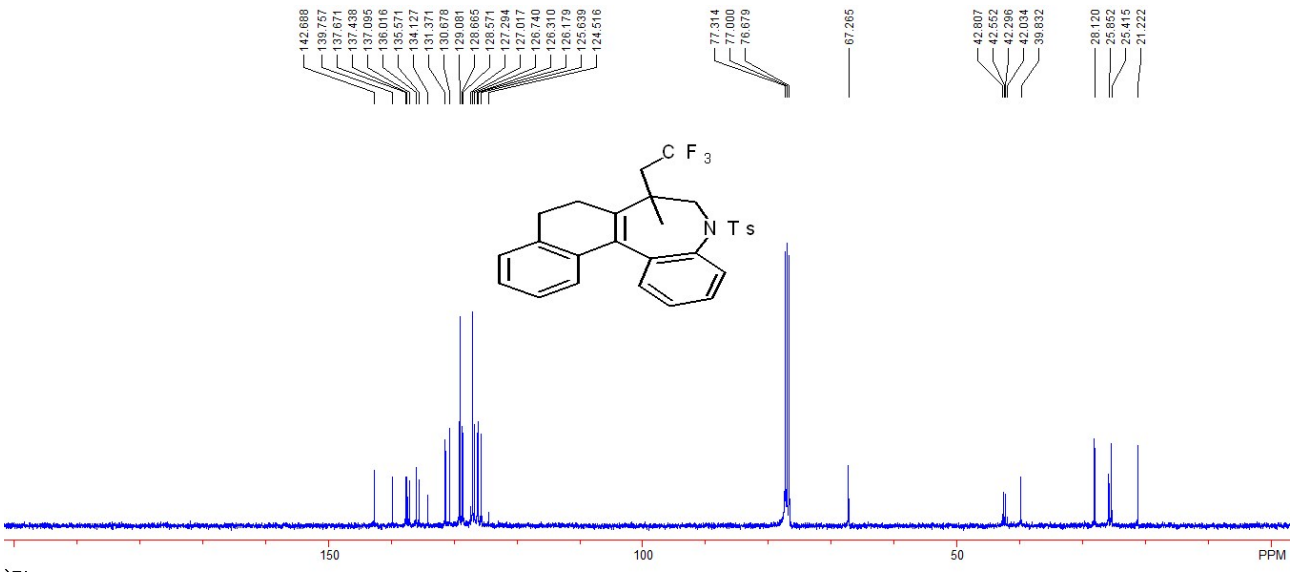
**1a** (0.15 mmol, 1.0 equiv), Togni reagent II (0.30 mmol, 2.0 equiv), CuTc (0.03 mmol, 0.20 equiv) were added to a Schlenk tube with a magnetic bar. MeCN (1.5 mL) was added and the reaction tube was heated to 60 °C for 12 h. The crude reaction mixture was diluted with EtOAc (5.0 mL) and the organic layer was washed with aqueous $NaHCO_3$ and brine. The mixture was extracted with EtOAc for 3 times. The organic layer was washed with brine and dried over anhydrous $Na_2SO_4$. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20 / 1) to afford the product **5** in 72% yield.

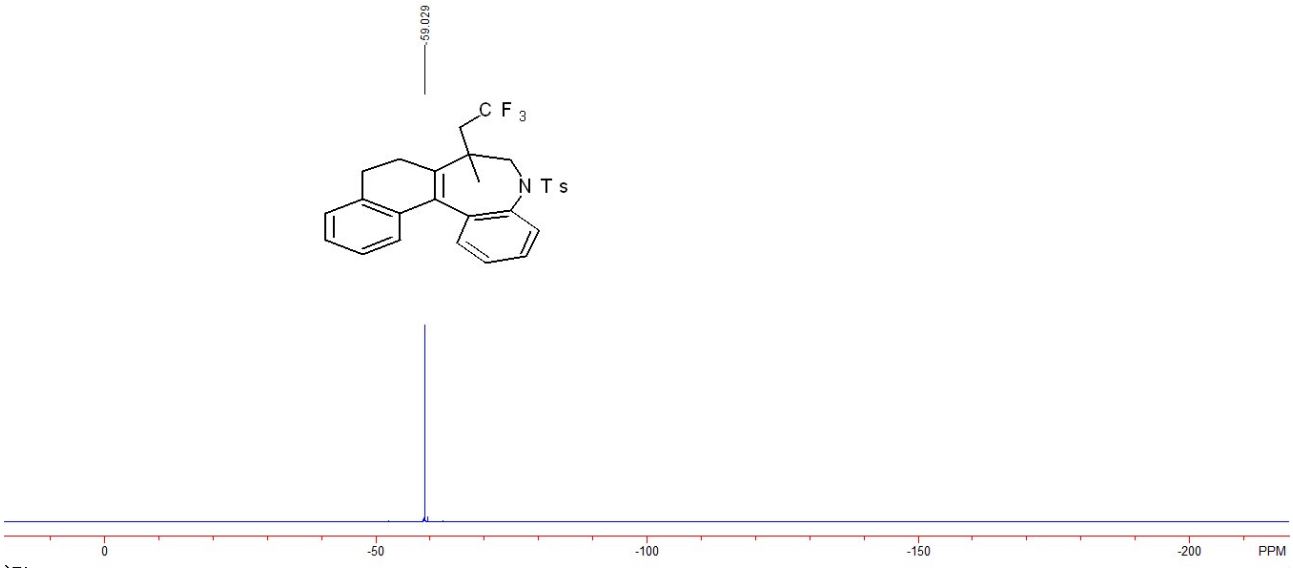
**Spectroscopic data for products 5**



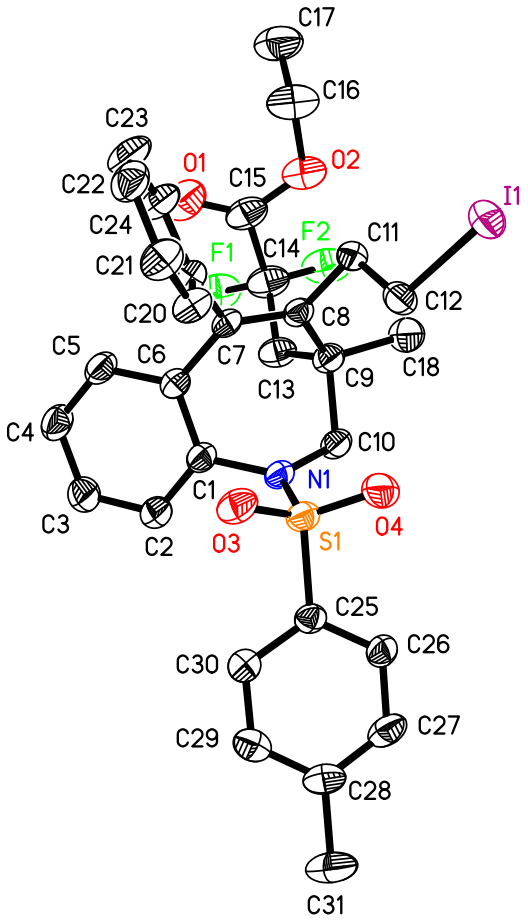

**Compound 5**: 54 mg, 72%, A white solid, m.p. 188-190 $^{o}$C; IR ($CH_2Cl_2$): ν 2979, 2942, 1487, 1347, 1259, 1163, 1103, 1091, 1042, 812, 782, 672 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$, TMS): δ 1.25 (s, 3H), 1.59-1.67 (m, 1H), 1.76-1.86 (m, 1H), 2.43-2.53 (m, 1H), 2.58 (s, 3H), 2.43-2.58 (m, 2H), 2.70 (td, 1H, $J_1$ = 16.0 Hz, $J_2$ = 5.6 Hz), 3.71 (d, 1H, $J$ = 14.0 Hz), 4.31 (d, 1H, $J$ = 14.0 Hz), 6.48 (d, 1H, $J$ = 7.6 Hz), 6.74 (d, 2H, $J$ = 7.6 Hz), 6.95 (t, 1H, $J$ = 7.2 Hz), 7.02-7.12 (m, 3H), 7.33-7.41 (m, 4H), 7.59 (d, 1H, $J$ = 8.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$, TMS): δ 21.2, 25.4, 25.9, 28.1, 39.8, 42.4 (q, $J_{C\text{-}F}$ = 25.6 Hz), 67.3, 125.6, 125.9 (q, $J_{C\text{-}F}$ = 277.8 Hz), 126.2, 126.3, 126.7, 127.0, 128.6, 128.7, 129.1, 130.7, 131.4, 134.1, 135.6, 136.0, 137.1, 137.4, 137.7, 139.8, 142.7; $^{19}F$ NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.0 (s); MS (ESI) *m/z*: 515.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{30}F_3N_2O_2S^+$ requires: 515.1975, Found: 515.1975.




142.688
139.757
137.671
137.438
137.095
136.016
135.571
134.127
131.371
130.678
129.081
128.865
128.571
127.294
127.017
126.740
126.310
126.179
125.639
124.516
77.314
77.000
76.679
67.265
42.807
42.552
42.296
42.034
39.832
28.120
25.852
25.415
21.222
C F 3
N Ts
150
100
50
PPM


59.029
C F 3
N Ts
0
-50
-100
-150
-200
PPM

**The crystal data of 2a**




The crystal data of **2a** have been deposited in CCDC with number 1440523. Empirical Formula: $C_{31}H_{32}F_2INO_4S$; Formula Weight: 679.53; Crystal Color, Habit: colorless, Crystal Dimensions: 0.220 x 0.170 x 0.130 $mm^3$; Crystal System: Monoclinic; Lattice Parameters: a = 14.4081(9)Å, b = 22.6704(15)Å, c = 19.5045(14)Å, α = 90°, β = 109.072(2)°, γ = 90°, V = 6021.2(7)$Å^3$; Space group: P 21/c; Z = 8; $D_{calc}$= 1.499 g/$cm^3$; $F_{000}$ = 2752; Final R indices [I>2sigma(I)] R1 = 0.0524, wR2 = 0.1316.

**Reference**


1 a) K. Utimoto, M. Tamura and K. Sisido, *Tetrahedron*, 1973, **29**, 1169; b) K. Chen, Z. Zhang, Y. Wei and M. Shi, *Chem. Commun.*, 2012, **48**, 7696; c) L.-Z. Yu, X.-B. Hu, Q. Xu and M. Shi, *Chem. Commun.*, 2016, **52**, 2701; d) L.-Z. Yu, Q. Xu, X.-Y. Tang and M. Shi, *ACS Catal.*, 2016, **6**, 526.

2 a) S. V. Frye, M. C. Johnson and N. L. Valvano, *J. Org. Chem.*, 1991, **56**, 3750; b) T. M. Acker, A. Khatri, K. M. Vance, C. Slabber, J. Bacsa, J. P. Snyder, S. F. Traynelis and D. C. Liotta, *J. Med. Chem.*, 2013, **56**, 6434.